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| U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE<br>(REV. 11-2000)  |  | ATTORNEY'S DOCKET NUMBER<br>11023-1                       |
| TRANSMITTAL LETTER TO THE UNITED STATES<br>DESIGNATED/ELECTED OFFICE (DO/EO/US)<br>CONCERNING A FILING UNDER 35 U.S.C. 371  |  | U S APPLICATION NO (If known, see 37 CFR 1.5<br>09/857701 |
| INTERNATIONAL APPLICATION NO.<br>PCT/CA00/00194   | INTERNATIONAL FILING DATE<br>28 February 2000 (28.02.00) | PRIORITY DATE CLAIMED<br>08 October 1999 (08.10.99)       |
| TITLE OF INVENTION<br>Cathode Active Material for Lithium Electrochemical Cells   |  |   |
| APPLICANT(S) FOR DO/EO/US<br>YOO, Yeong-Chang et al   |  |   |
| Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:   |  |   |
| <p>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.</p> <p>4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))</p> <p>a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</p> <p>b. <input type="checkbox"/> has been communicated by the International Bureau.</p> <p>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</p> <p>6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).</p> <p>a. <input type="checkbox"/> is attached hereto.</p> <p>b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</p> <p>7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))</p> <p>a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</p> <p>b. <input type="checkbox"/> have been communicated by the International Bureau.</p> <p>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</p> <p>d. <input type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</p> <p>10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p> |  |   |
| Items 11 to 20 below concern document(s) or information included:   |  |   |
| <p>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input type="checkbox"/> A <b>FIRST</b> preliminary amendment.</p> <p>14. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</p> <p>15. <input type="checkbox"/> A substitute specification.</p> <p>16. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</p> <p>18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</p> <p>19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</p> <p>20. <input type="checkbox"/> Other items or information:</p>  |  |   |

U.S. APPLICATION NO. 09/857701

INTERNATIONAL APPLICATION NO.  
PCT/CA/00194ATTORNEY'S DOCKET NUMBER  
11023-9821.  The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... \$1000.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$860.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$690.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$100.00

**ENTER APPROPRIATE BASIC FEE AMOUNT =**

\$ 860.00

Surcharge of \$130.00 for furnishing the oath or declaration later than  20  30 months from the earliest claimed priority date (37 CFR 1.492(e)).

\$ 130.00

| CLAIMS                                      | NUMBER FILED | NUMBER EXTRA | RATE       | \$       |
|---|--------------|--------------|------------|----------|
| Total claims                                | 22 - 20 =    | 2            | x \$18.00  | \$ 36.00 |
| Independent claims                          | 1 - 3 =      |              | x \$80.00  | \$       |
| MULTIPLE DEPENDENT CLAIM(S) (if applicable) |              |              | + \$270.00 | \$       |

**TOTAL OF ABOVE CALCULATIONS =**

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| <input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. | + | \$ |
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**SUBTOTAL =**

|  |    |
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| Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). | \$ |
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| <b>TOTAL NATIONAL FEE =</b> | \$ |
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| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property | + | \$ |
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| <b>TOTAL FEES ENCLOSED =</b> | \$ 1026.00 |
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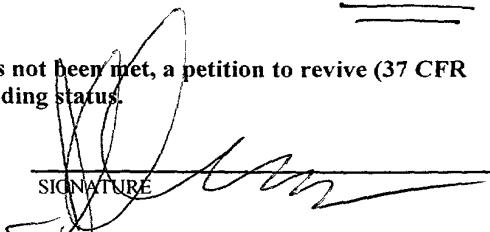
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- The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. \_\_\_\_\_. A duplicate copy of this sheet is enclosed.
- Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO

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PCT/CA00/00194

531 Rec'd PC

08 JUN 2001

## CATHODE ACTIVE MATERIAL FOR LITHIUM ELECTROCHEMICAL CELLS

### BACKGROUND OF THE INVENTION

This invention relates to a compound of molecular formula  $\text{Li}_x\text{Cr}_y\text{Mn}_{2-z}\text{O}_{4+z}$ , wherein  $2.2 < x < 4$ ,  $0 < y < 2$  and  $z \geq 0$ , and to the use of this compound as a cathode material in secondary lithium and lithium ion cells.

The impetus for this invention was the recent, great increase in demand for rechargeable batteries that combine high specific and volumetric energy density and with low cost and thermal stability.

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### DESCRIPTION OF THE PRIOR ART:

A lithium ion cell is a rechargeable electrochemical cell in which the electrochemically active components in both the cathode and the anode are lithium intercalation compounds. The intercalation compound serves as a host structure for lithium ions, which are either stored or released depending on the polarity of an externally applied potential. A lithium ion cell consists of a lithium intercalation cathode with an oxidizing potential and a lithium intercalation anode with a reducing potential. A lithium intercalation material is able to reversibly store and release lithium ions in response to an electrochemical potential. On discharge, in a lithium ion cell, lithium ions move from the anode to the cathode, and thereby, generate an electrochemical current. On charge, energy is consumed in forcing the lithium ions from the cathode to the anode. The greater the difference in the potentials of the cathode and the anode the greater the electrochemical potential of the resulting cell. The larger the amount of lithium which can be reversibly stored in and released from the cathode and the anode, the greater the capacity. The cell's discharge capacity reflects the time duration for which a cell can deliver a given current. Typical anodes for a lithium ion cell are made from carbonaceous materials such as graphite or petroleum cokes. Typical cathodes are made from transition metal oxides or sulphides.

For ease of cell fabrication, lithium ion cells are normally built in the fully discharged state with lithium present only in the cathode and not in the anode. In this state usually both the anode and the cathode materials are air stable. Assembling the cell in the discharged state means that the ultimate 5 capacity of the cell depends on the amount of lithium initially present in the cathode. For example, cathodes based on  $\text{LiMnO}_2$  have twice the theoretical capacity of cathodes based on  $\text{LiMn}_2\text{O}_4$ .

Previous reports and patents on cathodes for lithium ion cells have 10 proposed using various mixed oxides of lithium, such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  and  $\text{LiMn}_2\text{O}_4$  as the active material.

The use of phases such as  $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_{4.35}$  where  $0.2 < x < 0.4$ , and  $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$  where  $0 < x < 1$ , in secondary lithium batteries which have a 15 metallic lithium anode, are also known. See G. Pistoia et al, Solid State Ionics, 58, 285 (1992) and B. Wang et al, Studies of  $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$  for Secondary Lithium Batteries, extended Abstract from the Sixth International Meeting on Lithium Batteries, Munster, Germany, May 10-15, 1992. (See also J. Power Sources, 43-44, 539-546 (1992). The materials are 20 described in the latter case as being of a cubic lattice structure. Also in the latter case, additional Li was inserted electrochemically. However, only an additional 0.4 mole equivalents of lithium could be inserted e.g. to provide an oxide of molecular formula  $\text{Li}_{1.4}\text{Cr}_{0.4}\text{Mn}_{1.6}\text{O}_4$ .

25 Also, a lithium-poor lithium-manganese spinel structure for use in secondary electrochemical cells, having a molecular formula of  $\text{Li}_q\text{M}_x\text{Mn}_y\text{O}_z$  where q is 0 to 1.3, is described in US Patent No: 5,169,736.

More recently, the amount of lithium in such mixed metal oxides has been increased. In our previous US patent no. 5,370,949, issued 6 December 1994, a single phase compound of molecular formula  $\text{Li}_2\text{Cr}_x\text{Mn}_{2-x}\text{O}_4$ , wherein  $0 < x < 2$ , and its use in secondary lithium ion cells is described. These materials were prepared by standard solid state techniques and demonstrated good cycleability with discharge capacities up to 170 mAh/g at low current densities (3.6 mA/g). Higher discharge capacities were found for compositions in which at least half of the transition metal content was manganese. However phases with significantly more manganese than chromium developed a less commercially attractive two-plateau voltage curve on the first or subsequent discharges. Further structural and electrochemical characterization of these cathode materials was published by us in two papers in the Journal of Power Sources (volume 54, pages 205-208, in 1995 and volumes 81-82, pages 406-411, in 1999).

Another related material is described in US patent no. 4,567,031 of Riley, issued 28 January 1986. The abstract of this reference describes a mixed metal oxide having the formula  $\text{Li}_x\text{M}_y\text{O}_z$ , where M is at least one metal selected from the group consisting of titanium, chromium, manganese, iron, cobalt and nickel. It is significant that none of the enabled structures include Mn or Cr. Moreover, there is no enabled disclosure of the use of such compounds as cathodes for secondary cells.

Also, the preparation and characterization of materials of compositions  $\text{Li}_2\text{Cr}_x\text{Mn}_{2-x}\text{O}_4$  in which  $1.0 \leq x \leq 1.5$  was described by Dahn, Zheng and Thomas (J. Electrochem. Soc., 145, 851- 859, March 1998). These materials were made using a sol-gel technique followed by heating in an inert atmosphere to temperatures ranging from 500 to 1100 °C. In this study a maximum discharge capacity of 150 mAh/g at a low

current density (1.5 mA/g) was found for a sample of composition  $\text{Li}_2\text{Cr}_{1.25}\text{Mn}_{0.75}\text{O}_4$  which had been prepared at 700 °C. The same sample cycled at 15 mA/g showed a capacity of about 137 mAh/g. The materials prepared at 700 °C were all found by powder x-ray diffraction to have a 5 layered structure like  $\text{LiCoO}_2$  with a hexagonal unit cell symmetry. The volume of the crystallographic unit cells varied from 68.6 to 71.9 cubic angstroms per formula unit of  $\text{Li}_2\text{Cr}_x\text{Mn}_{2-x}\text{O}_4$ .

US Patent 5,858,324 issued January 12, 1999 discloses a process 10 for preparing a compound of formula  $\text{Li}_y\text{Cr}_x\text{Mn}_{2-x}\text{O}_{4+z}$  where  $y \geq 2$ ,  $0.25 < x < 2$  and  $z \geq 0$ . The experimental examples provided in the disclosure demonstrated the use of these materials as the active cathodes in rechargeable lithium ion electrochemical cells. The  $\text{Li}_y\text{Cr}_x\text{Mn}_{2-x}\text{O}_{4+z}$  samples were prepared as in the J. Electrochem. Soc. (145, 851- 859, March 15 1998) publication from chromium nitrate nonahydrate, manganese (II) acetate tetrahydrate and lithium hydroxide monohydrate by a sol-gel process using ammonium hydroxide as the gelling agent. The gels were heat treated in inert atmosphere at temperatures ranging from 500 to 1100 °C to form  $\text{Li}_y\text{Cr}_x\text{Mn}_{2-x}\text{O}_{4+z}$  compounds.

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The compounds were characterized by Reitveld refinement of crystallographic unit cell dimensions from powder x-ray diffraction data. The symmetry and space group of the compounds was found to depend on the composition and processing temperature. The structure 25 refinements and chemical analyses of the compositions studied are summarized in Table 1 of the patent (US 5,858,324). Table 1 of the patent (US 5,858,324) summarizes the structure refinements and chemical analyses for the 37 samples studied. Only two of the examples (samples 22 and 23) of  $\text{Li}_y\text{Cr}_x\text{Mn}_{2-x}\text{O}_{4+z}$  have compositions in which  $y$  is

greater than 2.0. The value of x ranges from 0.5 to 1.5 and the value of z as reported in table 6 is zero.

Only samples prepared at the lowest temperatures, 500 or 600 °C, 5 have crystallographic unit cell volumes per stoichiometric unit which are substantially smaller than that of  $\text{LiCrO}_2$  at 69.9 cubic Angstroms. Electrochemical characterization of these samples is not provided in the (US 5,858,324) patent disclosure. The compositions of  $\text{Li}_y\text{Cr}_x\text{Mn}_{2-x}\text{O}_{4+z}$  in examples 22 and 23 listed in table 1 of US 5,858,324 have y equal to 10 2.2 and x equal to 1.25. The crystallographic unit cell volumes per stoichiometric unit for example 22 which was prepared at 500 °C at 68.532 cubic Angstroms is significantly less than the 69.9 to 74.3 cubic Angstroms range provided for the same compounds as described in our previous US patent no. 5,370,949. Electrochemical characterization of 15 sample 22 is not provided in the US 5,858,324 patent. The electrochemical evaluation of Example 23 from US 5,858,324 which has a composition of  $\text{Li}_{2.2}\text{Cr}_{1.25}\text{Mn}_{0.75}\text{O}_4$  and a normalized unit cell volume of 69.81 cubic Angstroms is summarized in Table 6. The discharge capacity of this sample can be compared with that of example 3-3 in the same 20 table, which has a composition of  $\text{Li}_2\text{Cr}_{1.25}\text{Mn}_{0.75}\text{O}_4$ , a normalized crystallographic unit cell volume of 70.18 cubic Angstroms, and was tested under the same electrochemical conditions. Example 23 demonstrated a discharge capacity of 117 mAh/g only slightly better than 25 that of example 3-3 at 106 mAh/g. This small difference in the discharge capacities of the two examples falls within the normal range of variability between cells containing identical cathodes.

The US 5,858,324 patent was also filed as an international PCT application (WO 98/46528 and PCT US98/04940).

A similar material is described in Japanese Kokai 07,272,765, published 20 October 1995. In this reference, the mixed oxide is sintered with vanadium compounds to form a positive electrode material for a secondary cell.

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## SUMMARY OF THE INVENTION

It is an object of the present invention to provide novel lithium oxide materials for use as the active material in cathodes for lithium ion 10 electrochemical cells.

It is another object of the present invention to provide a secondary electrochemical cell of high energy density, whose charge/discharge mechanism is based upon alternating intercalation and deintercalation of  $\text{Li}^+$  15 ions in the active materials of the positive and negative electrodes.

It is a further objective of this invention to provide materials useful as cathodes in lithium ion cells that exhibit unusually large charge and discharge capacities.

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It is yet another object to provide good chemical resistance to the electrolyte and high cycling stability.

It is a further object of this invention to provide compounds 25 containing greater amounts of lithium. Increased lithium content provides additional paths for lithium ion mobility and increases the theoretical capacity of the cathode.

According to one aspect of the invention, a novel compound of 30 molecular formula I,



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wherein  $2.2 < x < 4.0$ ,  $0 < y < 2$  and  $z \geq 0$ , is provided.

While it is preferred that the value of  $x$  be in the range of about 2.2 to about 4, it is more preferred that  $x$  be in the range of 2.2 to 3.6.

Similarly, while it is more preferred that the value of  $y$  be in the middle and lower end of the range, i.e. about 0.1 to about 1.75, useful compounds according to the invention toward the upper end of the range, 10 i.e. up to about 1.9 are included.

In addition, it is preferred that  $z$  be  $> 0$ , it is more preferable that  $0 < z \leq 2.6$ .

15 The compounds of formula I may be further characterised by the crystallographic unit cell volume when indexed in hexagonal symmetry to a

R -3 m structure, being smaller than that of  $\text{LiCrO}_2$ , i.e. smaller than 104.9 cubic angstroms, and yet further characterized by the average 20 cation to anion bond distance being smaller than that of  $\text{LiCrO}_2$ . This value is available in the literature.

According to another aspect of the invention, the use of compounds 25 of molecular formula I as active cathode material in secondary lithium ion electrochemical cells is also provided.

According to yet another aspect of the invention, a secondary lithium ion electrochemical cell comprising a lithium intercalation anode, a suitable 30 non-aqueous electrolyte including a lithium salt, a cathode of a compound

of formula I as defined above as initial active material, and a separator between anode and cathode is provided.

According to a further aspect of the invention, several processes for 5 making the novel compounds of molecular formula I, are provided. The details of the processes are described below.

The anode of the present invention serves as the recipient for  $\text{Li}^+$  ions. Accordingly, the anode can be of any intercalation compound, which 10 is capable of intercalating lithium and has an electrode potential sufficiently reducing to provide an adequate cell voltage over a range of lithium intercalation. Specific examples include transition metal oxides such as  $\text{MoO}_2$  or  $\text{WO}_2$  [Auborn and Barberio, *J. Electrochem. Soc.* 134 638 (1987)], the disclosure of which is incorporated herein by reference, transition metal 15 sulfides (see also US Patent No: 4,983,476) or carbon products obtained by the pyrolysis of organic compounds. As will be apparent hereinafter, various commercially available carbonaceous materials of predetermined structural characteristics have proven useful.

20 The cathode of molecular formula I as defined above, is an intercalation compound with an electrochemical potential sufficiently positive of the anode to produce a useful overall cell voltage. The greater the potential, the greater the resulting energy density. The cathode generally serves as the initial reservoir of lithium. The capacity of the cell 25 will be limited by the amount of lithium, available for deintercalation, present in the cathode. In most cases, only a proportion of the lithium present, during fabrication of the cathode, can be reversibly deintercalated.

The non-aqueous electrolyte of the present invention can be liquid, 30 paste-like or solid. In particular, the electrolyte could be a solid or gelled

polymer. Polymers useful for electrolytes in lithium cells include polyvinylidene fluoride (PVDF), with and without co-polymers, and polyethylene oxide (PEO). The electrolyte typically includes a lithium salt in a liquid organic solvent. Lithium salts useful for this purpose include LiAsF<sub>6</sub>, 5 LiPF<sub>6</sub>, LiBF<sub>4</sub>, LiClO<sub>4</sub>, LiBr, LiAlCl<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiC(CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, and mixtures thereof. LiAsF<sub>6</sub> should be used with caution due to its toxicity. As a water-free solvent for these salts, there can be used alone or in mixture with others an organic solvent of the group propylene carbonate, ethylene carbonate, 2-methyl tetrahydrofuran, tetrahydrofuran, dimethoxyethane, 10 diethoxyethane, dimethyl carbonate, diethyl carbonate, methyl acetate, methylformate,  $\gamma$  - butyrolactone, 1,3-dioxolane, sulfolane, acetonitrile, butyronitrile, trimethylphosphate, dimethylformamide and other like organic solvents. The electrolyte solution can also contain additives such as Crown ethers eg. 12-C-4,15-C-5, and 18-C-6, or immobilising agents such as 15 polyethylene oxide or inorganic gel-forming compounds such as SiO<sub>2</sub>, or Al<sub>2</sub>O<sub>3</sub> such as described in US Patent No: 5,169,736, the disclosure of which is incorporated herein by reference.

#### BRIEF DESCRIPTION OF THE DRAWINGS

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FIG. 1 is a x-ray diffraction pattern of a sample prepared according to example 1.

FIGS. 2 to 6 show specific capacities versus voltage or cycle number for 25 electrochemical cells prepared according to example 1.

FIG. 7 overlays x-ray diffraction patterns of samples described in example 1.

FIGS. 8 and 9 show the voltage profiles of electrochemical cells prepared according to example 1.

FIG. 10 is a plot of capacity versus cycle number for an electrochemical cell cycled under the conditions described in example 1.

FIG. 11 is a x-ray diffraction pattern for the sample of example 2.

FIG. 12 provides the discharge voltage profiles of cells assembled and tested as described in example 2.

FIG. 13 is a SEM micrograph of a sample prepared according to example 2.

15 FIG. 14 is a plot of specific capacity for a cell prepared and tested as described in example 3.

FIGS. 15 – 16 are overlays of x-ray diffraction patterns of the samples prepared according to example 3.

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FIGS. 17 – 20 show specific capacities as a function of either voltage or cycle number for electrochemical cells prepared and tested according to example 4.

25 FIG. 21 is a x-ray diffraction pattern of a sample prepared as described in example 5.

FIG. 22 is a plot of voltage versus capacity for an electrochemical cell assembled and tested according to example 5.

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FIG. 23 is a x-ray diffraction pattern of a sample made according to example 6.

FIG. 24 shows SEM micrographs for samples described in example 6.

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FIGS. 25 – 26 are plots of specific capacities for electrochemical cells assembled and tested as described in example 6.

## 10 DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

The present invention relates to discovery of related phases with higher lithium content, and in some cases higher oxygen contents. As will be apparent from the examples which follow, these phases exhibit both a high capacity and a sloping, single-plateau voltage curve. They are 15 synthesized at temperatures in the range of 600 to 800 °C. Since they are prepared at moderate temperatures it is advisable to establish thoroughly homogeneous mixing of the precursors prior to firing. Consequently techniques which are known to be very effective at preparing homogeneous mixtures of fine powders have been employed. These 20 include co-precipitation, spray-drying and polymer complexation. All three of these techniques have been shown to work and are described in detail in the subsequent examples. The first two techniques were found to produce materials with exceptionally high capacities and rate capabilities.

25 In particular, the materials provided in this invention exhibit a large discharge capacity in a sloping, single-plateau voltage curve at potentials greater than 2.5 volts relative to the potential of metallic lithium.

The idea of these processes is to prepare a uniform mixture of finely divided metals salts, which can serve as precursors for the synthesis of lithiated transition metal oxides containing one or more transition metals. For example, in the spray drying process solutions of 5  $Mn(CH_3CO_2)_2$  and  $Cr_3(OH)_2(CH_3CO_2)_7$ , were employed. However any combination of water-soluble metal salts which can be decomposed thermally to the metal oxides could be used. Other suitable salts include metal nitrates, sulfates, hydroxides, oxyhydroxides, formates, citrates, and other organic salts. A lithium containing precursor such as lithium 10 hydroxide, lithium nitrate, lithium sulfate, lithium acetate, lithium carbonate, lithium oxide or lithium chloride could also be intimately mixed with the transition metal salts before thermal decomposition to the oxides. Alternatively, the lithium precursor can be reacted with the transition metal oxides prepared by thermal decomposition of the mixed 15 metal salts.

There are many ways to prepare homogeneous mixtures of fine powders, for example: sol-gel, co-precipitation, freeze drying, spray drying and others. Of these methods, co-precipitation has been widely used in 20 the field of Ni-MH battery for manufacturing spherical type  $Ni(OH)_2$  powder. In order to apply this technique to the Li system, initially composite hydroxides comprising Cr and Mn are made through co-precipitation of chromium and manganese hydroxides by adding an alkali aqueous solution to a mixed aqueous solution containing chromium and 25 manganese salts. Then the composite hydroxides are mixed with lithium compounds such as lithium hydroxide, lithium oxide or lithium carbonate and heat-treated at particular temperature range in an Argon atmosphere to make the cathode active material  $Li_xCr_yMn_{2-y}O_{4+z}$  where  $2.2 < x < 4$ ,  $0 < y < 2$  and  $z \geq 0$ .

Co-precipitation procedures can be used to prepare a range of  $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$  materials. The co-precipitation method starts by preparing mixed metal hydroxides from soluble metal salts such as nitrates, sulfates, acetates or chlorides. The metal salts are dissolved in de-ionized 5 water, and then mixed with an aqueous alkali solution under controlled conditions of temperature, pH, and concentration. The resulting metal hydroxides are mixed with a source of lithium such as lithium oxide, lithium hydroxide or lithium carbonate and fired at a variety of processing temperatures in an inert atmosphere. The heat treatment is used to 10 complete the reaction and to control the oxidation state of each transition metal. The oxidation states of the transition metals are critical to the material's crystal structure and electrochemical performance. The temperature of the heat treatment and the oxygen content within the reaction vessel will affect the oxidation states of the transition metals.

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For example, co-precipitation of a Cr-Mn composite hydroxide can be prepared as follows. An aqueous solution containing a mixture of water-soluble chromium and manganese salts such as chromium nitrate and manganese nitrate or chromic sulfate hydrate and manganese sulfate 20 is prepared by mixing the transition metal salts with de-ionized water. The co-precipitation of Cr hydroxide and Mn hydroxide is caused by controlled addition of an alkali aqueous solution containing an alkali such as ammonium hydroxide, potassium hydroxide, sodium hydroxide, lithium hydroxide or mixtures thereof into the aqueous solution of transition metal 25 salts. Then the Cr-Mn composite hydroxide is collected by filtering the deposits and rinsing them with water. The resulting composite hydroxide is then dried in an oven at 100°C. The dried composite hydroxide is then mixed with a source of lithium such as lithium oxide, lithium hydroxide or lithium carbonate and the mixture is heat-treated in Argon for 24 hours at 30 various temperatures between 600 and 1000°C. Characterization by

powder X-ray diffraction and typical electrochemical data for materials prepared by the co-precipitation method is provided in the example 4. The materials with the best electrochemical performance were those that were heat-treated at 650 – 750 °C.

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In a typical synthesis of  $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$  phases by the spray drying process solutions of metal salts were spray dried in a commercial spray dryer and then thermally decomposed to oxides at temperatures between 400 and 450 °C. The dried metal oxide powder was then reacted with a

10 lithium compound under controlled conditions. Suitable lithium

compounds include lithium oxides or any compounds that can be thermally decomposed to the oxide such as lithium hydroxide, lithium carbonate, lithium nitrate, lithium sulfate, or lithium acetate. The mixtures were carefully dried and calcined in air and then heat-treated in an argon

15 atmosphere to form the active cathode materials.

The compounds of formula I are further characterised by characteristic X-ray powder diffraction patterns. More specifically, the X-ray powder diffraction patterns of compounds of Formula I are similar to

20 that of  $\text{LiCrO}_2$  with the exception that the reflections are shifted to higher diffraction angles, corresponding to smaller crystallographic unit cell size. It can be expected that the volume of the crystallographic unit cell will decrease with increasing lithium content. The increase in lithium content is effectively a partial substitution of lithium atoms for transition metal atoms

25 and must be balanced by the partial oxidation of the remaining transition metals. The oxidation state of the manganese might, for example, be increased from +3 to +4 by the substitution of lithium atoms for transition metal atoms. This would result in a decrease in the

30 crystallographic unit cell volume because the weighted average of the ionic radii of the cations will have decreased. That is substituting  $\text{Li}^+$  and  $\text{Mn}^{+4}$  in

the 1:2 ratio, which would maintain charge balance, for  $\text{Cr}^{+3}$  or  $\text{Mn}^{3+}$  will result in a smaller average ionic radius.

The X-ray powder diffraction patterns of compounds of formula I 5 resemble the diffraction pattern of  $\text{LiCrO}_2$ , which has a hexagonal unit cell with a crystallographic structure belonging to the space group  $\text{R} -3 \text{ m}$ . Although the crystallographic structure of compounds of formula I have not been determined in detail, the X-ray diffraction patterns can be approximately indexed to hexagonal crystallographic unit cells like that of 10  $\text{LiCrO}_2$ . Comparison of crystallographic unit cell dimensions between related structures provides information about relative bond distances and oxidation states. Volumetric comparisons of related crystal structures are most useful between crystallographic volumes that contain the same number of atoms. Since  $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$  phases do not necessarily contain an equal number of 15 cations and anions, the quantity of cation or anion sites in the crystal structure must be chosen for making volumetric comparisons. After normalization to the same quantity of anion sites, the crystallographic unit cell volumes of  $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$  compounds are smaller than that of  $\text{LiCrO}_2$ .

20 For example,  $\text{LiCrO}_2$  has a hexagonal unit cell with  $a = 2.899 \text{ \AA}$  and  $c = 14.412 \text{ \AA}$  (ICDD card # 24-600), and the X-ray powder diffraction pattern of  $\text{Li}_3\text{Cr}_{1.1}\text{Mn}_{0.9}\text{O}_{4.1}$  (from example 2) can be indexed to a hexagonal unit cell with  $a = 2.876 \text{ \AA}$  and  $c = 14.253 \text{ \AA}$ . The corresponding crystallographic unit cell volumes are  $104.9 \text{ \AA}^3$  for  $\text{LiCrO}_2$  and  $102.1 \text{ \AA}^3$  for 25  $\text{Li}_3\text{Cr}_{1.1}\text{Mn}_{0.9}\text{O}_{4.1}$  based on a hexagonal  $\text{R} -3\text{m}$  structure. Similarly  $\text{Li}_{3.1}\text{Cr}_{1.34}\text{Mn}_{0.66}\text{O}_{5.8}$  from Table 4 in the examples to follow has a crystallographic unit cell volume of  $102.92 \text{ \AA}^3$ . In comparison, the crystallographic unit cell volume of  $\text{Li}_2\text{CrMnO}_4$  for a similar number of atomic sites is  $107.69 \text{ \AA}^3$  (J. Power Sources, vol. 81-82, p. 406-411, 30 1999).

The invention relates to a compound having the formula  $\text{Li}_x\text{Cr}_y\text{Mn}_z$ <sub>2</sub> $\text{O}_{4+z}$  wherein  $2.2 < x < 4$ ,  $0 < y < 2$ , and  $z \geq 0$  and an electrode composition containing this compound. In the embodiment of the 5 invention in which the compound is used as the active agent in an electrode, the initial composition has the formula  $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$  wherein  $2.2 < x < 4$ ,  $0 < y < 2$ , and  $z \geq 0$ , and in the course of utilizing the compound as an electrode, the composition can vary in x from 4 to 0.

10 As indicated above, while it is preferred that the value of x be in the upper end of the range, i.e. about 2.2 to about 4, and more preferably in the range of 2.5 to 3.6, useful intermediate compounds through the middle of the range where x is about 2, to the lower end of the range where x is near 0 are also within the scope of this invention.

15 As will be apparent hereafter, these intermediate compounds are formed by cycling an appropriate cell starting with a cathode of a material of formula I in which x is about 2.2 to about 4.

20 In the utilization of materials as electrodes structural changes often occur during the electrochemical cycling such that the initial structure is not necessarily maintained. In the examples to follow the change in shape of the voltage profile of the charge curve after the first charge suggests that a substantial structural change may have occurred.

25 As will be shown in the examples, to follow, compounds of the present invention have exceptionally good chemical stability. Greater chemical stability often results in enhanced safety in electrochemical cells. For example, see US Patent Nos: 4,983,276, 4,956,248, and 4,110,696.

The preferred negative electrode is based on a carbonaceous product.

Suitable carbonaceous materials include:

1) carbonaceous material with a  $d_{002}$  layer spacing of less than or equal to 3.70 Å with true density of greater than or equal to 5 1.70 g/cm<sup>3</sup> prepared by carbonization of furan resins, as per US Patent No: 4,959,281.

2) the above doped with 2-5 % phosphorous and oxygenated petroleum or coal pitch carbonized and doped with 2-5 % phosphorous with the same  $d_{002}$  layer spacing and true density, as per 10 published European application No: EP 0 418 514.

3) carbons formed by the thermal decomposition of gas phase hydrocarbons or hydrocarbon compounds with  $d_{002}$  from 3.37 to 3.55 Å as per US Patent No: 4,863,814.

4) carbon formed from mesophase microspheres with  $d_{002}$  15 layer spacing up to 3.45 Å as per US Patent No: 5,153,082.

5) commercial petroleum coke, as per US Patent No: 4,943,497.

6) isotropic graphite composed of a mixture of graphite and carbonized pitch with a degree of graphitization greater than or equal to 20 0.4 and heat treated fluid coke and commercial graphite whose first lithium electrochemical intercalation is performed at or above 50°C, as per US Patent No: 5,028,500.

(The disclosure of the aforementioned 6 references are incorporated herein by reference).

25

Typical electrodes in the present invention are fabricated from 70 - 94 weight percent of active material, graphitic carbon or  $Li_xCr_yMn_{2-y}O_{4+z}$ , 5 - 20 weight percent of a conductivity enhancer such as *Super S* carbon black and/or graphite, and 1-10 weight percent of a binder such as 30 poly(vinylidene fluoride) (PVDF) or Kynar Flex®.

Other conductivity enhancers such as Shawinigan Acetylene Black, graphites or other conductive materials may be used. In addition, other binders such as Teflon®, ethylene propylene diene monomer (EPDM), 5 polyolefins or elastomers may be substituted for Kynar Flex.

It will be apparent from the examples, which follow that the compounds of the invention have the following distinguishing characteristics. They contain a greater molar percentage of lithium than 10 previously known related materials and therefore have a greater theoretical capacity in use as cathodes in a lithium ion cells. They are characterized by their composition, crystallographic unit cell dimensions, x-ray diffraction patterns, and shape of their voltage curves. When used as cathodes in secondary lithium or lithium ion cells, the compounds of 15 the invention exhibit significant enhancement in discharge capacities relative to related cathode materials. In addition, secondary lithium or lithium ion cells with cathodes based on the compounds of the invention exhibit a broader operational voltage range. It is expected that a broader operational voltage range will facilitate higher currents and faster 20 recharging times.

#### Example 1

For example, a solution containing (12.30 g, 0.05 moles) of 25 manganese acetate tetrahydrate,  $Mn(CH_3CO_2)_2 \cdot 4H_2O$  (Aldrich), and (10.05 g, ~0.0167 moles) of chromium acetate hydroxide,  $Cr_3(OH)_2(CH_3CO_2)_7$  (Aldrich), dissolved in 500 ml of de-ionized water was dried in a commercial (Buchi 190) mini spray-drier. The dried metal acetate mixture was calcined in air at 400 °C for 3 hours. A mass of 2.8 g of this oxide 30 was slurried with 13 ml of a 4M solution of lithium hydroxide in de-

ionized water and heated treated in an alumina crucible in a tube furnace under a flow of air. The heating regime was controlled to heat the sample slowly, over 5.5 hours, to 450 °C, hold at 450 °C for 2 hours and then allow the sample to cool slowly in the furnace to room temperature.

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The sample was reground and then fired in a tube furnace at 700°C for 3 hours under in a flow of argon gas. Figure 1 is a x-ray diffraction pattern of the sample after heat-treatment. The diffraction pattern can be compared to that of  $\text{LiCrO}_2$  as indicated by the bar diagram under the 10 diffraction pattern. The diffraction pattern of the  $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$  sample is similar to that of  $\text{LiCrO}_2$  but there are differences in the relative intensities of the peaks and the peaks of  $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$  are shifted to higher angle relative to those of  $\text{LiCrO}_2$ . Chemical analysis of the sample by atomic absorption found the composition to be 15  $\text{Li}(3.30\pm0.25)\text{Mn}(1.06\pm0.08)\text{Cr}(0.94\pm0.05)\text{O}(5.54\pm0.28)$ , with the oxygen content estimated by difference.

The material was cast into an electrode sheet and tested in coin cells. Electrodes were prepared from a mixture of 0.456 g of active 20 material, 0.047 g of Super S carbon black, and 0.049 g of graphite (Lonza KS4). The mixture was formed into a slurry with 1.206 g of a binder solution containing 3 weight percent of Kynar Flex 2801 in n-methyl pyrrolidinone (NMP) and cast as a film on aluminum foil by the doctor blade method. The cast was dried in air at low heat on a hot plate 25 and then at 110 °C for twenty minutes in a convection oven. Electrode discs of 1.27 cm diameter were punched from the cast and densified by pressing each disc with a force of 500 lbs. on a hydraulic press. The electrodes typically had a thickness between 0.008 to 0.013 cm after pressing.

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The electrochemical cycling was carried out in 2325 coin cells each containing an internal spring and spacer to maintain an adequate pressure on the electrode stack. The anodes were lithium (Foote Mineral) discs of 1.65 cm diameter and 0.05 cm thickness and electrolyte containing 1 M 5 LiPF<sub>6</sub> in 1:1 ethylene carbonate (EC) : dimethyl carbonate (DMC) (Mitsubishi Chemical).

The voltage profile for the first seven cycles of a cell cycled at 3.6 mA/g between 2.5 and 4.3 volts is shown in figure 2. The initial 10 discharge capacity was 180 mAh/g and the average output voltage was 3.41 volts. A plot of discharge capacity versus cycle number for this cell is provided in figure 3. Another cell cycled between 2.5 and 4.5 volts produced discharge capacities of 187 to 200 mAh/g at 3.6 mA/g and 145 to 147 mAh/g at 14.4 mA/g as shown in figure 4. Figure 5 is a plot of 15 capacity versus cycle number for a similar cell cycled at 7.2 mA/g from 2.5 volts to initially 4.3 volts and later 4.5 volts. This cell demonstrated only moderate capacity fade over 75 cycles and discharge capacities of up to 179 mAh/g. Figure 6 shows the discharge capacity versus cycle number for a cell cycled between 2.5 and 4.3 volts for the first cycle and 20 between 2.5 and 4.5 volts for subsequent cycles at 3.6 mA/g. The cell demonstrated very good capacity retention over 30 cycles at discharge capacities over 195 mAh/g.

A portion of the sample was washed with water to remove any 25 soluble residuals and some of this material was cast and tested in coin cells. Atomic absorption analysis of the material after washing corresponded to the composition Li(3.15±0.32)Mn(1.11±0.11)Cr(0.89±0.06)O(5.00±0.31), with the oxygen content estimated by difference. Figure 7 shows a comparison of

the powder x-ray diffraction patterns of the material before and after washing.

An electrode cast was made of the washed sample in a similar 5 manner as the unwashed sample. The electrode cast of the washed sample contained 0.406 g active material, 0.050 g Super S, 0.054 g graphite and 1.286 g of a 3 weight percent solution of Kynar Flex 2801 in NMP. Electrodes discs were punched from this cast and tested in coin 10 cells in a manner similar to the previous examples. This cast was used in a cell cycled at 7.2 mA/g between 2.5 and 4.5 volts. The cell had a discharge capacity of 182 mAh/g on the first cycle. Figure 8 shows the capacity and voltage profile of this cell. A voltage versus capacity plot for another cell containing a cathode punched for the same cast is shown 15 in figure 9. This cell was cycled at 3.6 mA/g between 2.5 and 4.7 volts on the first cycle and between 2.75 and 4.7 volts for subsequent cycles. Figure 10 is a plot of discharge capacity versus cycle number for the same cell. As can be seen in the figure this cell could be cycled to 4.7 volts over 30 cycles without severe capacity loss and retained discharge capacities in excess of 185 mAh/g.

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The atomic absorption analyses of both the washed and unwashed samples verify that they contain greater amounts of lithium and oxygen than  $Li_2Cr_yMn_{2-y}O_4$  phases. Comparison of the powder x-ray diffraction patterns of these samples to that of  $LiCrO_2$  clearly indicates a smaller 25 crystallographic unit cell. Cycling to 4.7V has proven successful using either  $LiPF_6$  or  $LiBF_4$  electrolyte solutions.

**Example 2**

In this example, an intimate mixture of manganese and chromium salts was prepared by spray drying a 1 liter solution containing 24.677 g 5 of manganese acetate (Aldrich) and 22.075 g of chromium acetate hydroxide (Aldrich). The metal salts were calcined at 475 °C for 4 hours in air. A quantity of the product of the calcination, 4.014 g, was combined with 20.85 ml of a 4 M aqueous solution of LiOH (Anachemia) as a slurry. The mixture was slowly heated to 450°C in air and held at 10 that temperature for 2 hours. After cooling the sample was ground by hand with a mortar and pestle and then transferred to an alumina boat for a final heat treatment in a flow of argon at 700 °C for 4 hours. The x-ray diffraction pattern of this sample is shown in figure 11. A Rietveld refinement of the diffraction pattern calculated the crystallographic unit 15 cell dimensions to be 2.876 Å in the a and b directions and 14.25 Å in the c direction of a hexagonal symmetry cell. The volume of the crystallographic unit cell is calculated to be 102.1 cubic Angstroms, significantly lower than that of  $\text{LiCrO}_2$  at 104.9 cubic Angstroms. A chemical analysis by atomic absorption predicted a composition of 20  $\text{Li}_{2.95}\text{Mn}_{0.91}\text{Cr}_{1.09}\text{O}_{4.11}$  for this sample.

After grinding again by hand a portion of the material was formed into an electrode cast by combining 0.465 g of active material with 0.051 g of Super S carbon black, 0.052 g of graphite (Lonza KS4) and 1.131 g of a 4 weight percent solution of Kynar Flex 2801 in NMP. Cathode discs 25 cut from this cast were tested in coin cells similar to those described in the prior examples. Figure 12 shows the voltage versus capacity profiles for cells with these cathodes cycled at the indicated current densities. The charge and discharge capacities at the 1<sup>st</sup>, 15<sup>th</sup>, 30<sup>th</sup> and 50<sup>th</sup> cycles for cells cycled at various current densities are tabulated in table 1. Two

SEM micrographs of the product from the spray-drying procedure are provided in figure 13.

Table 1 – Charge and discharge capacities for the 1<sup>st</sup>, 15<sup>th</sup>, 30<sup>th</sup> and 50<sup>th</sup> cycle of cells cycled between 2.5 and 4.5 volts at the indicated current densities.

| Cell   | Active Mass | Current | Ch/Dis Cap 1st | Ch/Dis Cap 15th | Ch/Dis Cap 30th | Ch/Dis Cap 50th |
|--------|-------------|---------|----------------|-----------------|-----------------|-----------------|
|        |             | mA/g    | Mah/g          | mAh/g           | mAh/g           | MAh/g           |
| CTCD56 | 0.0171      | 3.6     | 280/216        | 213/207         |                 |                 |
| CTCD57 | 0.0168      | 4.8     | 270/205        | 202/196         |                 |                 |
| CTCD58 | 0.0171      | 7.2     | 260/198        | 192/190         | 201/196         |                 |
| CTCD59 | 0.0171      | 7.2     | 265/187        | 196/181         | 204/188         |                 |
| CTCD60 | 0.0162      | 14.4    | 249/178        | 177/168         | 176/162         | 176/166         |
| CTCD61 | 0.0174      | 14.4    | 247/177        | 170/163         | 168/160         | 162/154         |
| CTCD62 | 0.0175      | 28.8    | 227/159        | 145/143         | 147/144         | 141/136         |
| CTCD63 | 0.0174      | 14.4    | 245/183        | 171/170         | 169/168         | 160/159         |
|        |             |         |                |                 |                 |                 |

### Example 3

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The effect of increasing the concentration of Cr and Mn metals, for 20 stoichiometries ranging from  $\text{Li}_x\text{Mn}_{1.5}\text{Cr}_{0.5}\text{O}_{4+z}$  to  $\text{Li}_x\text{Mn}_{0.5}\text{Cr}_{1.5}\text{O}_{4+z}$ , was studied using the spray drying process.

15 Solutions of varied concentration of  $\text{Mn}(\text{CH}_3\text{CO}_2)_2$  and  $\text{Cr}_3(\text{OH})_2(\text{CH}_3\text{CO}_2)_7$  were prepared, spray dried in a commercial Buchi

spray drier and then thermally decomposed at 450°C. The dried oxides were mixed with a 4 M solution of LiOH in a ratio of 1 g of oxide to 5.2 ml of LiOH solution. The resulting slurry was dried and calcined in air by slowly heating it to 450 °C and holding it at 450 °C for 2 hours. The 5 material was ground by hand with an agate mortar and pestle and transferred to an alumina crucible before heating at 700°C for 4 to 5 hours under a blanket of flowing argon gas. The target and chemically analyzed compositions are listed in tables 2 and 3 for the chromium-rich and manganese-rich samples respectively. The chemical analysis was 10 done by atomic absorption and the oxygen compositions are calculated by difference. The uncertainty in the chemical analysis by atomic absorption was approximately 5 to 8 mole %. The discharge capacities of cells cycled between 2.5 and 4.5 volts at a current density of 7.2 mA/g are listed in tables 2 and 3 for the 1<sup>st</sup>, 10<sup>th</sup> and 20<sup>th</sup> cycles.

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On cycling the phases with a higher concentration of Cr (designated as chromium-rich) first discharge capacities of up to 221 mAh/g were observed. The cell with a cathode of composition,  $\text{Li}_{3.1}\text{Cr}_{1.05}\text{Mn}_{0.95}\text{O}_{5.4}$ , demonstrated a stable capacity near 180 mAh/g over 20 50 cycles at 7.2 mA/g as shown in figure 14. Cells with cathodes of compositions  $\text{Li}_{3.1}\text{Cr}_{1.10}\text{Mn}_{0.90}\text{O}_{5.1}$ ,  $\text{Li}_{3.3}\text{Cr}_{1.20}\text{Mn}_{0.80}\text{O}_{4.9}$  and  $\text{Li}_{2.8}\text{Cr}_{1.46}\text{Mn}_{0.54}\text{O}_{5.2}$  also showed very stable capacities of 180 and 170 mAh/g at the same current density. The x-ray diffraction patterns of chromium-rich samples A to J are overlaid in figure 15.

Table 2 – Compositions and discharge capacities of Cr-rich  $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$ 

| Sample | Target    | Composition analysis  | Li/O  | Discharge Capacity (mAh/g) |
|--------|-----------|---|-------|----------------------------|
|        | Cr/Mn     | atomic absorption   |       | Cycle: 1, 10, 20           |
| A      | 1.05/0.95 | $\text{Li}_{2.9}\text{Mn}_{0.99}\text{Cr}_{1.01}\text{O}_{5.4}$ | 0.539 | 152,158,165                |
| B      | 1.10/0.90 | $\text{Li}_{3.1}\text{Mn}_{0.95}\text{Cr}_{1.05}\text{O}_{5.4}$ | 0.569 | 179,186,191                |
| C      | 1.15/0.85 | $\text{Li}_{3.1}\text{Mn}_{0.90}\text{Cr}_{1.10}\text{O}_{5.1}$ | 0.604 | 171,178,182                |
| D      | 1.20/0.80 | $\text{Li}_{3.4}\text{Mn}_{0.85}\text{Cr}_{1.15}\text{O}_{5.7}$ | 0.584 | 189,153,133                |
| E      | 1.25/0.75 | $\text{Li}_{3.3}\text{Mn}_{0.80}\text{Cr}_{1.20}\text{O}_{4.9}$ | 0.683 | 215,180,180                |
| F      | 1.30/0.70 | $\text{Li}_{3.1}\text{Mn}_{0.75}\text{Cr}_{1.25}\text{O}_{5.4}$ | 0.571 | 188,132,113                |
| G      | 1.35/0.65 | $\text{Li}_{3.2}\text{Mn}_{0.69}\text{Cr}_{1.31}\text{O}_{5.1}$ | 0.623 | 193,135,113                |
| H      | 1.40/0.60 | $\text{Li}_{3.3}\text{Mn}_{0.66}\text{Cr}_{1.34}\text{O}_{5.9}$ | 0.564 | 197,143,150                |
| I      | 1.45/0.55 | $\text{Li}_{3.1}\text{Mn}_{0.59}\text{Cr}_{1.41}\text{O}_{5.0}$ | 0.619 | 180,125,120                |
| J      | 1.50/0.50 | $\text{Li}_{2.8}\text{Mn}_{0.54}\text{Cr}_{1.46}\text{O}_{5.2}$ | 0.550 | 221,162,171                |

The x-ray diffraction patterns of the manganese-rich series of samples 5 A to J are shown in figure 16. The discharge capacities for the 1<sup>st</sup>, 10<sup>th</sup> and 20<sup>th</sup> cycles of cells with cathodes based on the manganese-rich materials cycled between 2.5 and 4.5 volts at a current density of 7.2 mA/g are listed in table 3. The manganese-rich materials exhibited very stable discharge capacities over the first twenty cycles. A cell with a cathode of composition 10  $\text{Li}_{3.1}\text{Mn}_{1.07}\text{Cr}_{0.93}\text{O}_{6.6}$  had a capacity of 175 mAh/g on the 20<sup>th</sup> cycle while those of compositions  $\text{Li}_{2.8}\text{Mn}_{1.10}\text{Cr}_{0.90}\text{O}_{4.5}$  and  $\text{Li}_{3.1}\text{Mn}_{1.15}\text{Cr}_{0.85}\text{O}_{4.7}$  had capacities of 145 and 150 mAh/g by the 20<sup>th</sup> cycle.

Table 3 – Compositions and discharge capacities of Mn-rich  $\text{Li}_x\text{Cr}_y\text{Mn}_2$  $\text{O}_{4+z}$ 

| Sample | Target    | Composition analysis  | Li/O  | Discharge Capacity (mAh/g) |
|--------|-----------|---|-------|----------------------------|
|        | Mn/Cr     | atomic absorption   |       | Cycle: 1, 10, 20           |
| A      | 1.05/0.95 | $\text{Li}_{2.8}\text{Mn}_{1.10}\text{Cr}_{0.90}\text{O}_{4.5}$ | 0.632 | 147,141,145                |
| B      | 1.10/0.90 | $\text{Li}_{3.1}\text{Mn}_{1.07}\text{Cr}_{0.93}\text{O}_{6.6}$ | 0.463 | 148,169,175                |
| C      | 1.15/0.85 | $\text{Li}_{3.1}\text{Mn}_{1.15}\text{Cr}_{0.85}\text{O}_{4.7}$ | 0.653 | 141,144,150                |
| D      | 1.20/0.80 | $\text{Li}_{3.2}\text{Mn}_{1.17}\text{Cr}_{0.83}\text{O}_{4.5}$ | 0.708 | 100,117,126                |
| E      | 1.25/0.75 | $\text{Li}_{3.3}\text{Mn}_{1.22}\text{Cr}_{0.78}\text{O}_{4.6}$ | 0.720 | 89,96,101                  |
| F      | 1.30/0.70 | $\text{Li}_{2.8}\text{Mn}_{1.30}\text{Cr}_{0.70}\text{O}_{4.9}$ | 0.575 | 89,115,118                 |
| G      | 1.35/0.65 | $\text{Li}_{2.9}\text{Mn}_{1.36}\text{Cr}_{0.64}\text{O}_{4.9}$ | 0.591 | 122,130,132                |
| H      | 1.40/0.60 | $\text{Li}_{3.0}\text{Mn}_{1.40}\text{Cr}_{0.60}\text{O}_{5.3}$ | 0.552 | 87,102,108                 |
| I      | 1.45/0.55 | $\text{Li}_{3.0}\text{Mn}_{1.46}\text{Cr}_{0.54}\text{O}_{5.4}$ | 0.550 | 87,121,108                 |
| J      | 1.50/0.50 | $\text{Li}_{2.9}\text{Mn}_{1.51}\text{Cr}_{0.49}\text{O}_{5.0}$ | 0.582 | 128,122,120                |

5

**Example 4**

The effect of increasing the lithium content was studied using the 10 spray-drying procedure. Two samples were prepared in as in examples 1 and 2 except that the ratio of lithium hydroxide solution to calcined metal salts was increased. Atomic absorption analysis of the first and second of these samples determined the compositions to be  $\text{Li}_{3.48}\text{Mn}_{0.96}\text{Cr}_{1.04}\text{O}_{4.80}$  and  $\text{Li}_{3.61}\text{Mn}_{0.97}\text{Cr}_{1.03}\text{O}_{5.49}$  respectively. These samples were formed into

The Cr-Mn double hydroxide was obtained by filtering the deposits and the rinsing with water. The water rinsing was repeated while continuously measuring the pH value until the pH reached 6-7. The resulting double hydroxide was dried at 100°C in air. Other precursors 5 such as chromium sulfate and manganese sulfate may also be used as the source of Cr and Mn, respectively. Any combination of metal salts that can make an aqueous solution is usable. Potassium hydroxide, ammonium hydroxide and lithium hydroxide may be used as the caustic alkali solution.

10 A firing process using a Li compound is described as follows.

Lithium hydroxide was used as the Li compound. The Cr-Mn double hydroxide obtained through the co-precipitation method described above was mixed with lithium hydroxide, and the mixture was placed in an alumina crucible and fired in a horizontal tube furnace under a flow of 15 argon gas. The sample was fired for 24 hours at 650 - 700°C. After the firing the product was gradually cooled to room temperature and milled to a powder to be used as the cathode active material.

After preparing several active materials of various Li/Cr/Mn ratios, each sample was examined by an X-ray diffraction method. The cathodes 20 were prepared by casting and drying a slurry made from 85wt% active material with 10wt% acetylene black and 5wt% polyvinylidene fluoride (PVdF) in NMP. The substrate was Al foil and the diameter of punched cathodes was 10 mm. The anodes were prepared by punching lithium metal film, having the thickness of 0.8 mm and the diameter of 12 mm. 25 The diameters of the electrodes were chosen to fit a commercial coin cell case of the type #2016. These coin cells have a diameter of 20 mm and a height of 1.6 mm.

The cell stack consisted of a three-layer sandwich of the cathode, a cell separator, and a lithium anode. The separator used was a 30 polypropylene film. The electrolyte used was a 50/50 mixture by volume

electrodes and electrochemically evaluated in coin cells as in the previous examples. Figure 17 is a plot of voltage versus capacity for the first of these samples for the first three cycles of a cell cycled between 2.5 and 4.5 volts at 3.6 mA/g. The discharge capacities of the first three cycles 5 were 222, 237 and 233 mAh/g of active cathode material. Figure 18 is a plot of discharge capacity versus cycle number for the same cell. As can be seen in the figure a capacity near 215 mAh/g was sustained for more than 40 cycles. The same sample was also evaluated in another coin cell at a higher current density. Figure 19 plots the discharge capacity for the 10 first 100 cycles of a cell cycled between 2.5 and 4.5 volts at a current density of 14.4 mA/g. A discharge capacity near 150 mAh/g was maintained for 100 cycles. The second sample was tested in a similar manner as previous examples. A coin cell with a cathode comprised of the second sample was cycled between 2.5 and 4.5 volts at 3.6 mA/g. 15 The discharge capacity of the first 32 cycles as shown in figure 20 is, after the first few cycles, remarkably constant at about 210 mAh/g.

#### Example 5

20

A process for preparing a Cr-Mn hydroxide through co-precipitation according to present invention is described. An aqueous solution of 2M concentration in chromium nitrate was prepared by adding a specified quantity (according to the targeted Cr/Mn ratio) of manganese nitrate to 25 the solution with the final composition adjusted using water. Slowly pouring caustic alkali aqueous solution containing 6 M sodium hydroxide into the concentrated transition metal nitrate solution caused the co-precipitation of Cr hydroxide and Mn hydroxide. The precipitation was finished when the pH of the mixed solution reached a value of 10.

The Cr-Mn double hydroxide was obtained by filtering the deposits and the rinsing with water. The water rinsing was repeated while continuously measuring the pH value until the pH reached 6-7. The resulting double hydroxide was dried at 100°C in air. Other precursors 5 such as chromium sulfate and manganese sulfate may also be used as the source of Cr and Mn, respectively. Any combination of metal salts that can make an aqueous solution is usable. Potassium hydroxide, ammonium hydroxide and lithium hydroxide may be used as the caustic alkali solution.

10 A firing process using a Li compound is described as follows.

Lithium hydroxide was used as the Li compound. The Cr-Mn double hydroxide obtained through the co-precipitation method described above was mixed with lithium hydroxide, and the mixture was placed in an alumina crucible and fired in a horizontal tube furnace under a flow of 15 argon gas. The sample was fired for 24 hours at 650 - 700°C. After the firing the product was gradually cooled to room temperature and milled to a powder to be used as the cathode active material.

After preparing several active materials of various Li/Cr/Mn ratios, each sample was examined by an X-ray diffraction method. The cathodes 20 were prepared by casting and drying a slurry made from 85wt% active material with 10wt% acetylene black and 5wt% polyvinylidene fluoride (PVdF) in NMP. The substrate was Al foil and the diameter of punched cathodes was 10 mm. The anodes were prepared by punching lithium metal film, having the thickness of 0.8 mm and the diameter of 12 mm. 25 The diameters of the electrodes were chosen to fit a commercial coin cell case of the type #2016. These coin cells have a diameter of 20 mm and a height of 1.6 mm.

The cell stack consisted of a three-layer sandwich of the cathode, a cell separator, and a lithium anode. The separator used was a 30 polypropylene film. The electrolyte used was a 50/50 mixture by volume

of ethylene carbonate and dimethyl carbonate containing 1M LiPF<sub>6</sub>. The cells were assembled and crimped in a helium filled glove box. The coin cells were charged and discharged with the current density of 3.6 mA/g and the voltage range was 4.3-2.5V.

5 Figure 21 shows the X-ray diffraction pattern of Li<sub>x</sub>CryMn<sub>2-y</sub>O<sub>4+z</sub> (x = 2.65, y = 0.75, z = 1.86). Figure 22 shows the charge and discharge curves of active material having above formula. Table 4 represents the results of charge and discharge capacity of several different formulas. The atomic ratios of Li, Cr, and Mn were determined  
10 by AA analysis. Oxygen contents were determined by difference. The lattice parameters: a, b and c are in Angstrom units and the unit cell volumes are in units of cubic Angstroms.

Table 4. Typical examples from co-precipitation process

| No. | Li mole (x) | Cr mole (y) | Mn mole (2-y) | O mole (z) | 1 <sup>st</sup> ch/disch (mAh/g) | 5 <sup>th</sup> disch (mAh/g) | Crystal structure (a, c, unit cell volume)  |
|-----|-------------|-------------|---------------|------------|----------------------------------|-------------------------------|---|
| 1   | 2.65        | 1.25        | 0.75          | 1.86       | 240.12/<br>201.94                | 204.01                        | Hexagonal<br>a = 2.885<br>c = 14.250<br>v = 102.77                                  |
| 2   | 2.25        | 1.23        | 0.77          | 0.37       | 229.76/<br>194.69                | 177.92                        | Hexagonal<br>a = 2.891<br>c = 14.288<br>v = 103.42                                  |
| 3   | 3.44        | 1.22        | 0.78          | 1.55       | 278.17/<br>204.93                | 191.65                        | Hexagonal<br>a = 2.875<br>c = 14.211<br>v = 101.78                                  |
| 4   | 3.09        | 1.34        | 0.66          | 1.79       | 283.81/<br>229.69                | 202.19                        | Hexagonal<br>a = 2.891<br>c = 14.216<br>v = 102.92                                  |
| 5   | 2.74        | 0.98        | 1.02          | 1.06       | 230.25/<br>188.28                | 182.98                        | Hexagonal<br>a = 2.893<br>c = 14.223<br>v = 103.16                                  |
| 6*  | 2.65        | 1.25        | 0.75          | 1.58       | 241.18/<br>147.12                | 133.05                        | Hexagonal<br>a = 2.889<br>c = 14.253<br>v = 103.03                                  |
| 7*  | 3.01        | 0.99        | 1.01          | 0.12       | 238.76/<br>157.39                | 126.80                        | Monoclinic<br>a = 5.197<br>b = 2.861<br>c = 5.213<br>$\beta$ = 112.17°<br>v = 71.79 |
| 8*  | 1.98        | 1.20        | 0.80          | 0.07       | 207.07/<br>147.76                | 121.17                        | Monoclinic<br>a = 5.153<br>b = 2.871<br>c = 5.184<br>$\beta$ = 111.45°<br>v = 71.41 |
| 9*  | 2.04        | 0.51        | 1.49          | 0.13       | 176.00/<br>119.93                | 97.37                         | Hexagonal<br>a = 2.909<br>c = 14.442<br>v = 105.84                                  |

(\* No.1 sample heated at 800°C, \*\* samples made by solid state process)

**Example 6**

Another sample was prepared by the co-precipitation process described in example 5 using chromium sulfate,  $\text{Cr}_2(\text{SO}_4)_3 \times \text{H}_2\text{O}$ , and 5 manganese sulfate,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ , instead of nitrate salts. The precipitation of the mixed transition metal hydroxide was initiated by the controlled addition of ammonium hydroxide. The mixed hydroxide was combined with lithium hydroxide monohydrate and heated at 650 °C in a flow of argon gas for 24 hours. A x-ray diffraction pattern of the product is 10 provided in figure 23.

Scanning electron micrographs comparing samples prepared by the co-precipitation process using either nitrate or sulphate salts to those prepared at 1000 °C by a solid state process are provided in figure 24.

15 Figure 25 and 26 are plots of discharge capacity versus cycle number for four cells containing cathodes comprised of compounds made by the co-precipitation process from either nitrate or sulfate salts. All the cells were cycled between voltage limits of 2.5 to 4.3 volts. The two in figure 25 20 were cycled at 3.6 mA/g while those in figure 26 were tested at a current density of 14.5 mA/g. The compositions as determined from atomic absorption are indicated in the figures 24 through 26.

## WE CLAIM:

1. A compound of molecular formula I,



wherein  $2.2 < x < 4$ ,  $0 < y < 2$  and  $z \geq 0$ .

2. A compound according to Claim 1, wherein formula I,

$2.2 < x < 4$  and  $0.1 \leq y \leq 1.75$ .

3. A compound according to Claim 1, wherein formula I,

$2.2 < x < 3.6$  and  $0.1 \leq y \leq 1.75$ .

4. A compound according to Claim 1, further characterised by the normalised crystallographic unit cell volume, when indexed in hexagonal symmetry to a R-3m structure, being smaller than that of  $\text{LiCrO}_2$  ie. smaller than 104.9 cubic Angstroms.

5. A compound according to Claim 1, further characterised by the average cation to anion bond distance being smaller than that of  $\text{LiCrO}_2$ .

6. A compound according to Claim 1, wherein formula I,  $x = 2.8$  to  $3.4$ ,  $y = 0.49$  to  $1.46$  and  $z = 0.5$  to  $2.6$ .

7. A compound according to Claim 1, wherein formula I,  $x = 2.8$  to  $3.4$ ,  $y = 1.01$  to  $1.46$  and  $z = 0.9$  to  $1.9$ .

8. A compound according to Claim 1, wherein formula I,  $x = 2.8$  to  $3.3$ ,  $y = 0.49$  to  $0.93$  and  $z = 0.5$  to  $2.6$ .
9. A compound according to Claim 1, wherein formula I,  $x = 2.04$  to  $3.44$ ,  $y = 0.51$  to  $1.34$  and  $z = 0.07$  to  $1.86$ .
10. A compound according to Claim 1, wherein formula I,  $x = 2.25$  to  $3.44$ ,  $y = 0.98$  to  $1.34$  and  $z = 0.37$  to  $1.86$ .
11. A compound according to Claim 1, wherein formula I,  $x = 3.15$  to  $3.30$ ,  $y = 0.89$  to  $1.09$  and  $z = 1.00$  to  $1.54$ .
12. A compound according to Claim 1, wherein formula I,  $x = 2.95$ ,  $y = 1.09$  and  $z = 0.11$ , further characterised by a normalised unit cell volume of  $102.1$  cubic angstroms and being indexed to a hexagonal crystallographic unit cell having dimensions  $a = 2.876$  angstroms,  $b = 2.876$  angstroms, and  $c = 14.25$  angstroms.
13. A cathode for use in a secondary lithium ion electrochemical cell, comprising as active material a compound of formula I as defined in Claim 1.
14. A secondary lithium ion electrochemical cell comprising, a lithium intercalation anode, a suitable non-aqueous electrolyte including a lithium salt, a cathode as defined in Claim 13, and a separator between the anode and cathode.
15. An electrochemical cell according to Claim 14, wherein the anode comprises a material selected from the group consisting of transition metal oxides, transition metal

sulphides and carbonaceous materials, and wherein the electrolyte is in liquid form and includes a suitable organic solvent.

16. An electrochemical cell according to Claim 15, wherein the lithium salt is selected from the group consisting of LiAsF<sub>6</sub>, LiPF<sub>6</sub>, LiBF<sub>4</sub>, LiClO<sub>4</sub>, LiBr, LiAlCl<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiC(CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, and mixtures thereof.
17. An electrochemical cell according to Claim 16, wherein the organic solvent is selected from the group consisting of propylene carbonate, ethylene carbonate, 2-methyl tetrahydrofuran, tetrahydrofuran, dimethoxyethane, diethoxyethane, dimethyl carbonate, diethyl carbonate, methyl acetate, methylformate,  $\gamma$ -butyrolactone, 1,3-dioxolane, sulfolane, acetonitrile, butyronitrile, trimethylphosphate, dimethylformamide and other like organic solvents and mixtures thereof.
18. An electrochemical cell according to Claim 17, wherein the anode comprises a carbonaceous material.
19. An electrochemical cell according to Claim 18, wherein the anode comprises a graphitic carbon.
20. An electrochemical cell according to Claim 18, wherein the electrolyte is a solid or gelled polymer.

21. An electrochemical cell according to Claim 18, wherein the electrolyte comprises 1 M LiPF<sub>6</sub> in a 1:1 mixture of ethylene carbonate and dimethyl carbonate.
22. An electrochemical cell according to Claim 19, wherein formula I, x = 2.2 to 4, y = 0.1 to 1.75 and z ≥ 0 .

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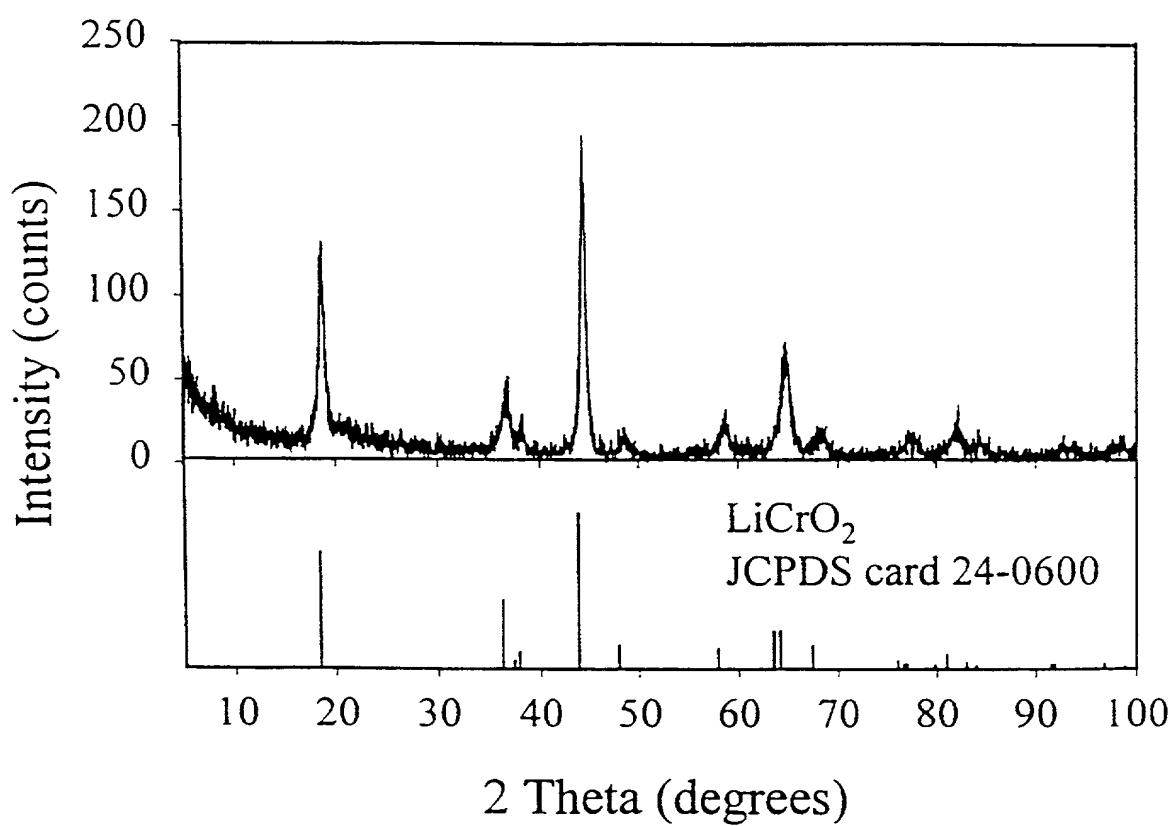


Figure 1

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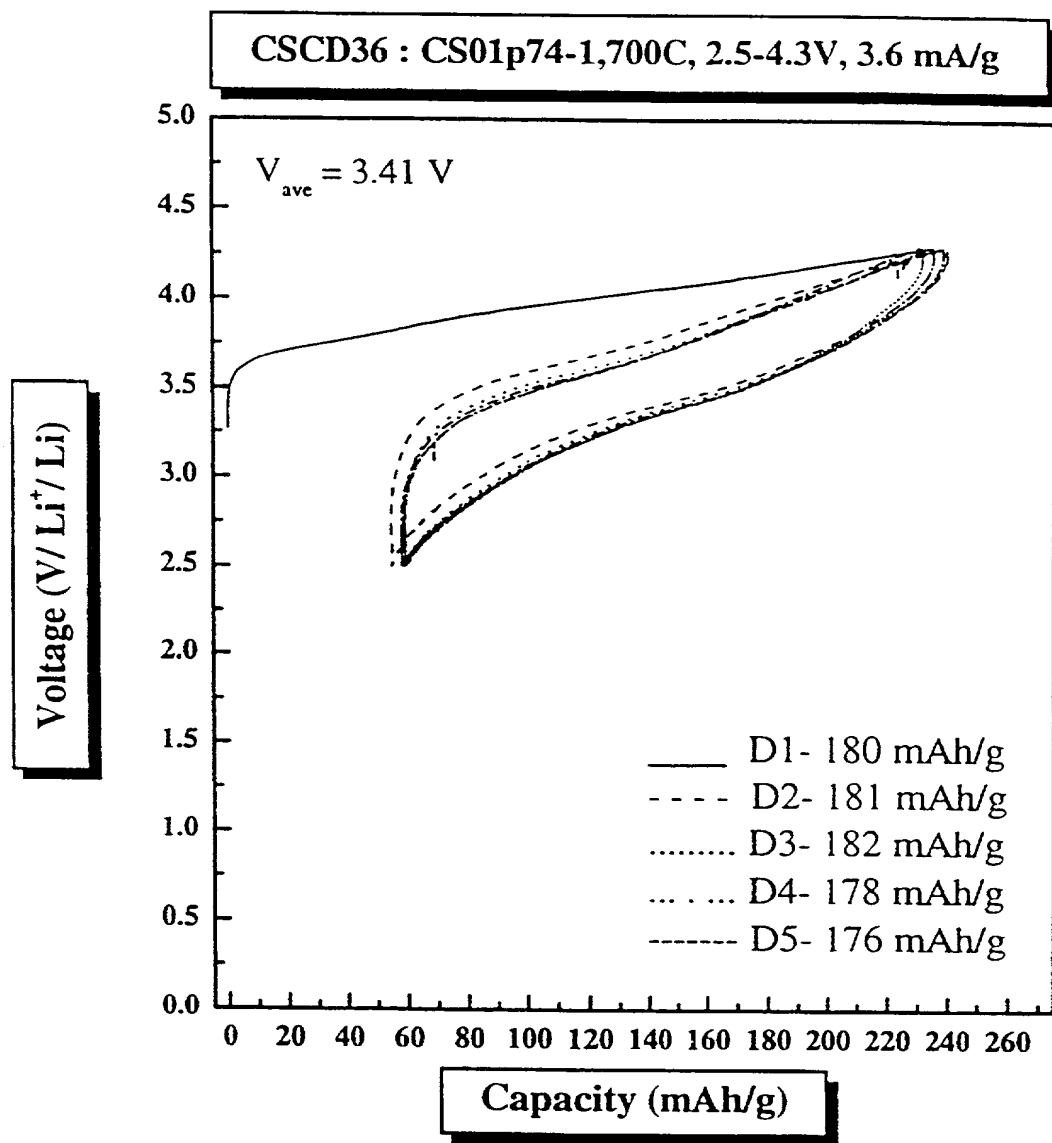


Figure 2

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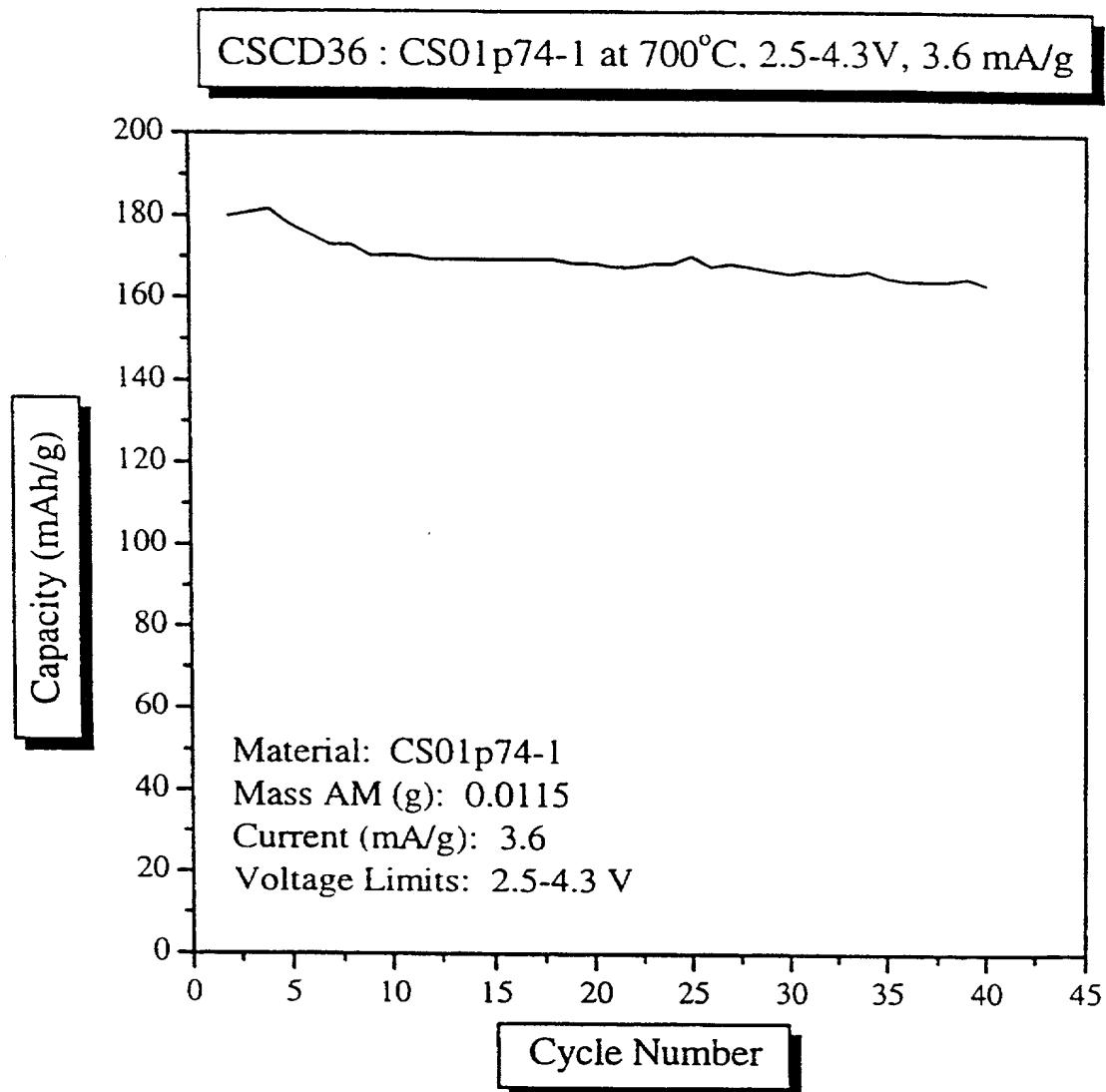


Figure 3

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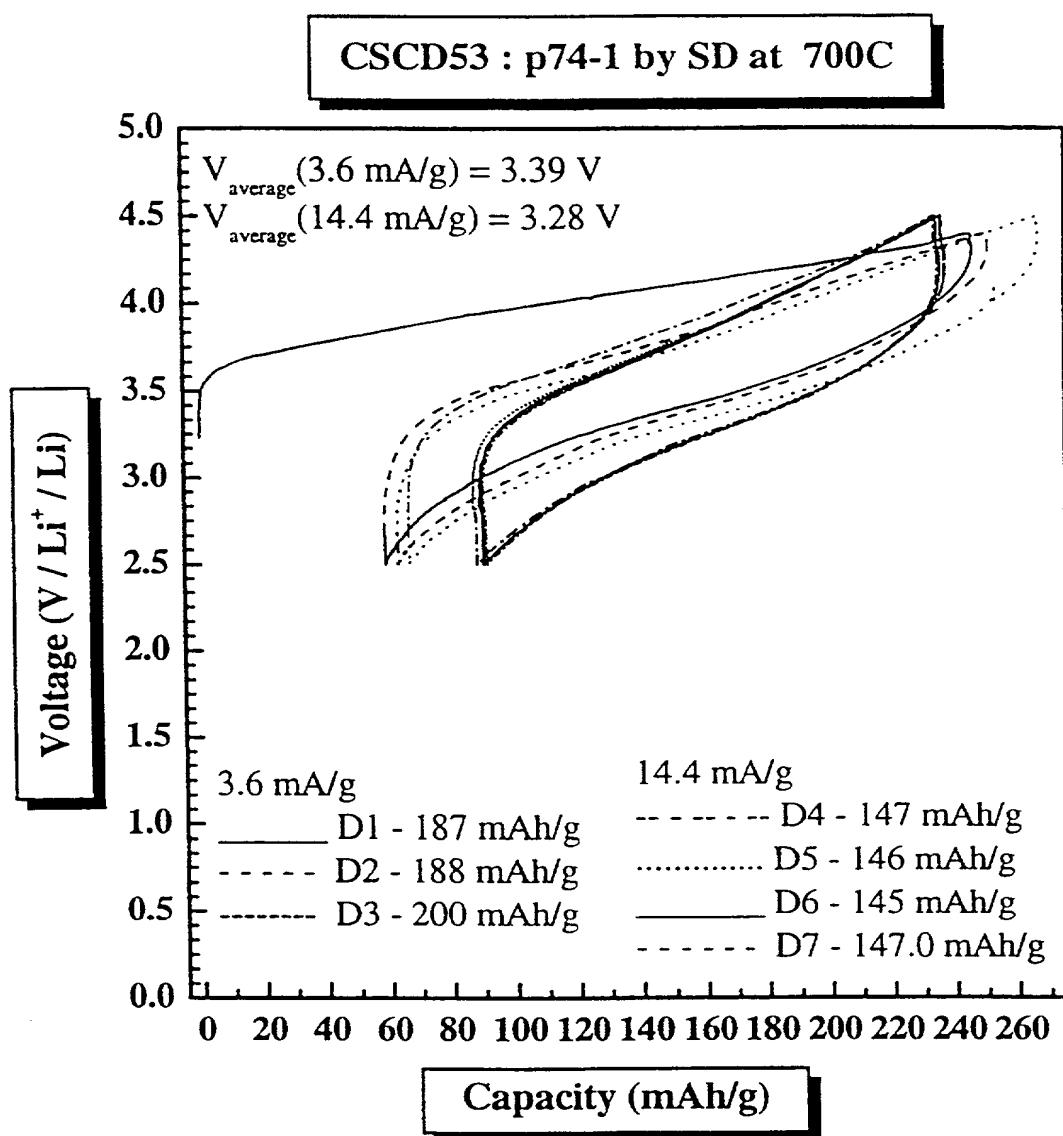


Figure 4

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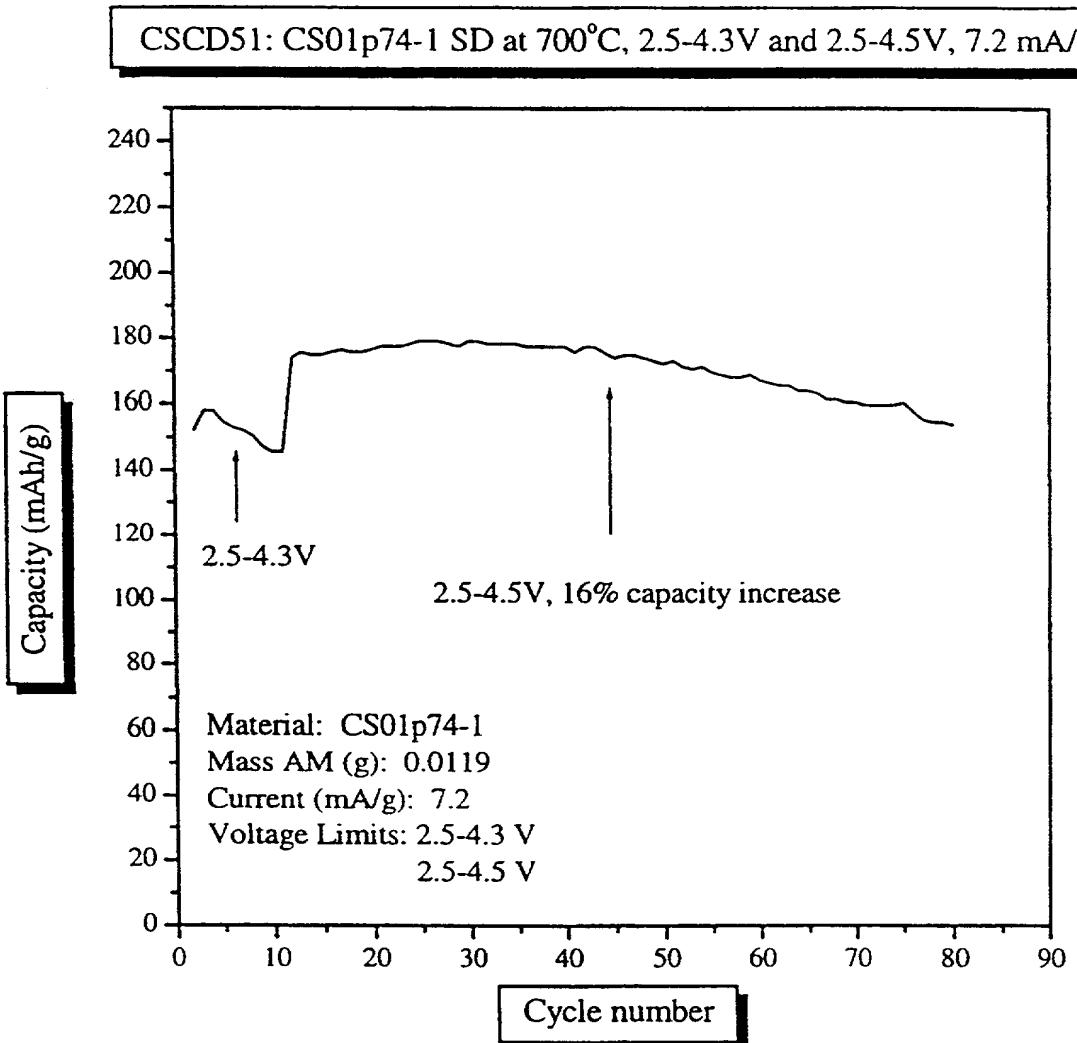


Figure 5

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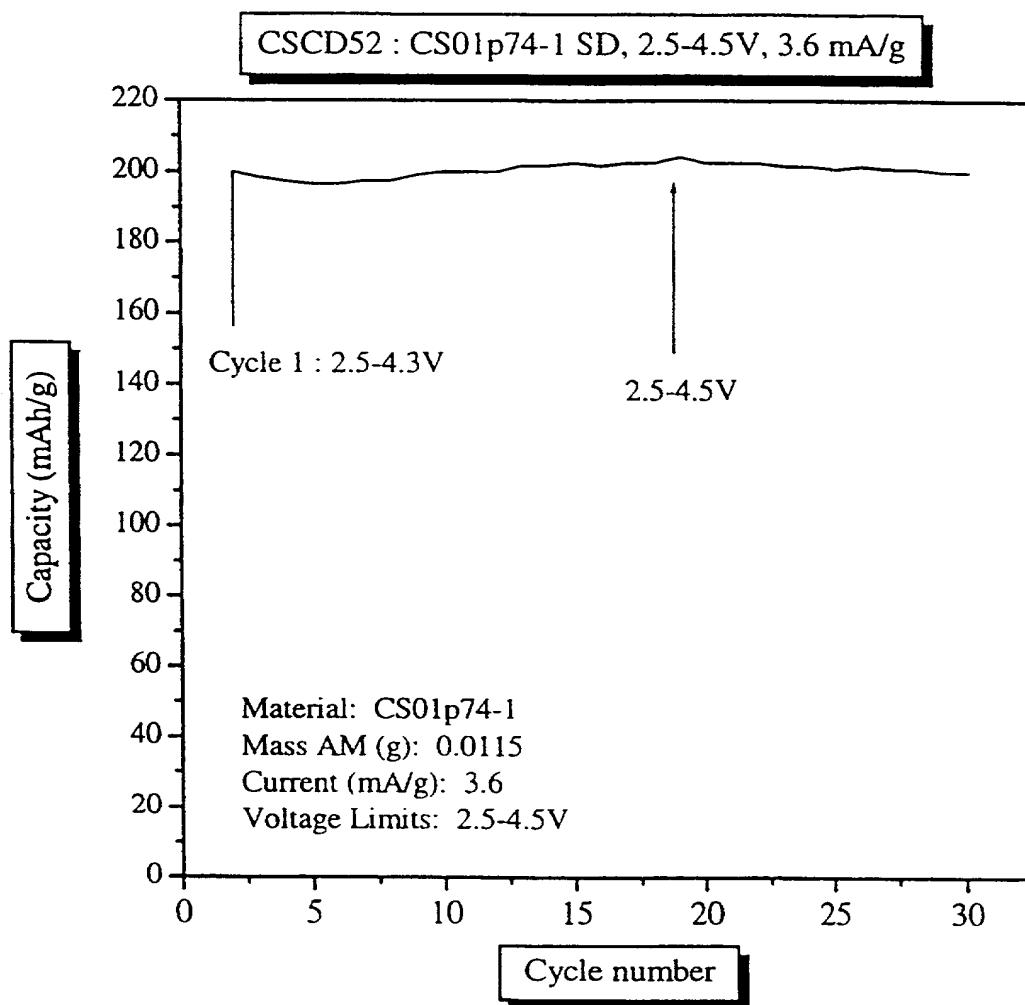


Figure 6

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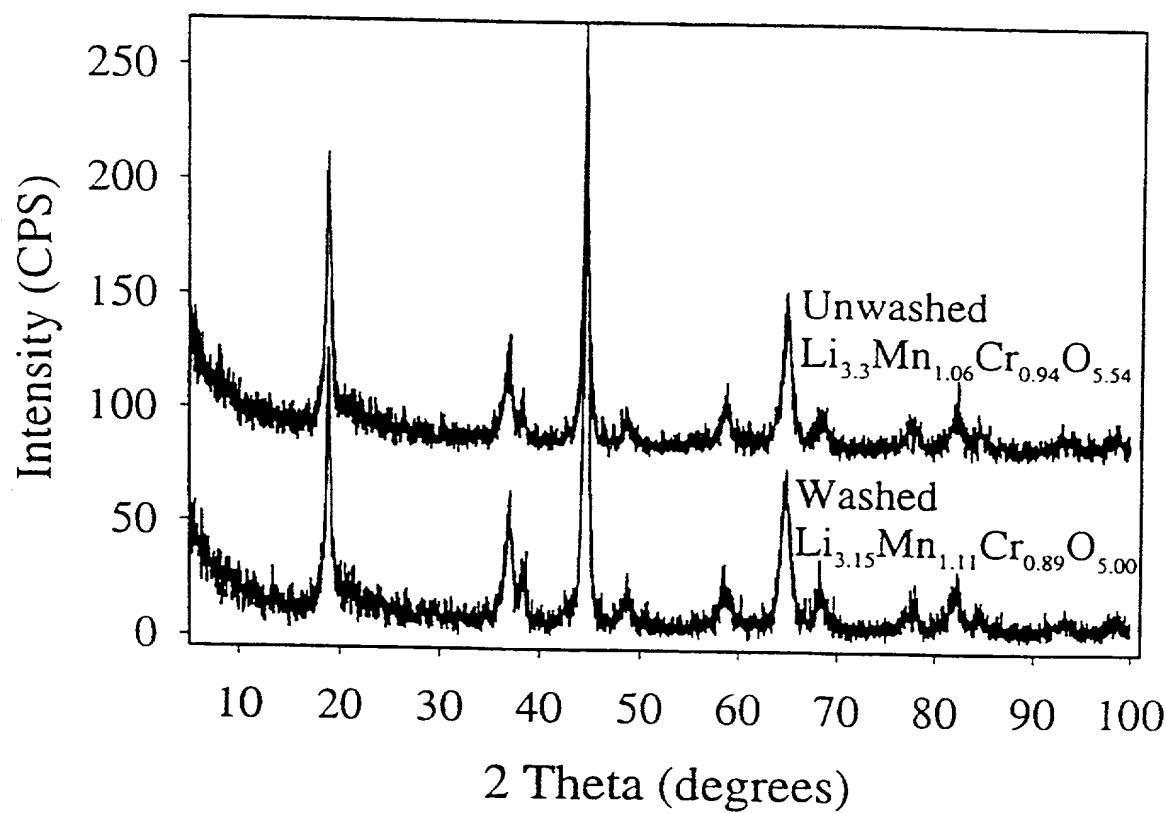


Figure 7

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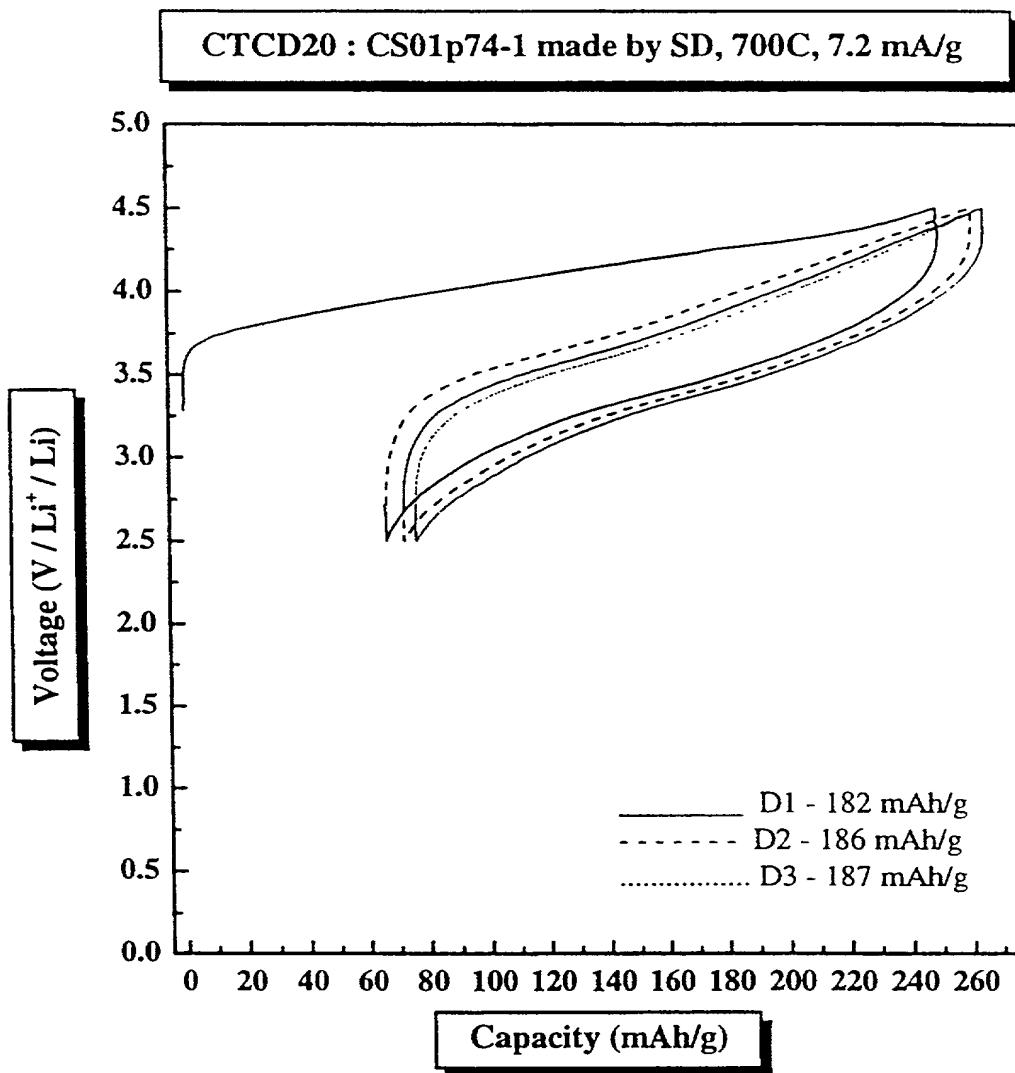


Figure 8

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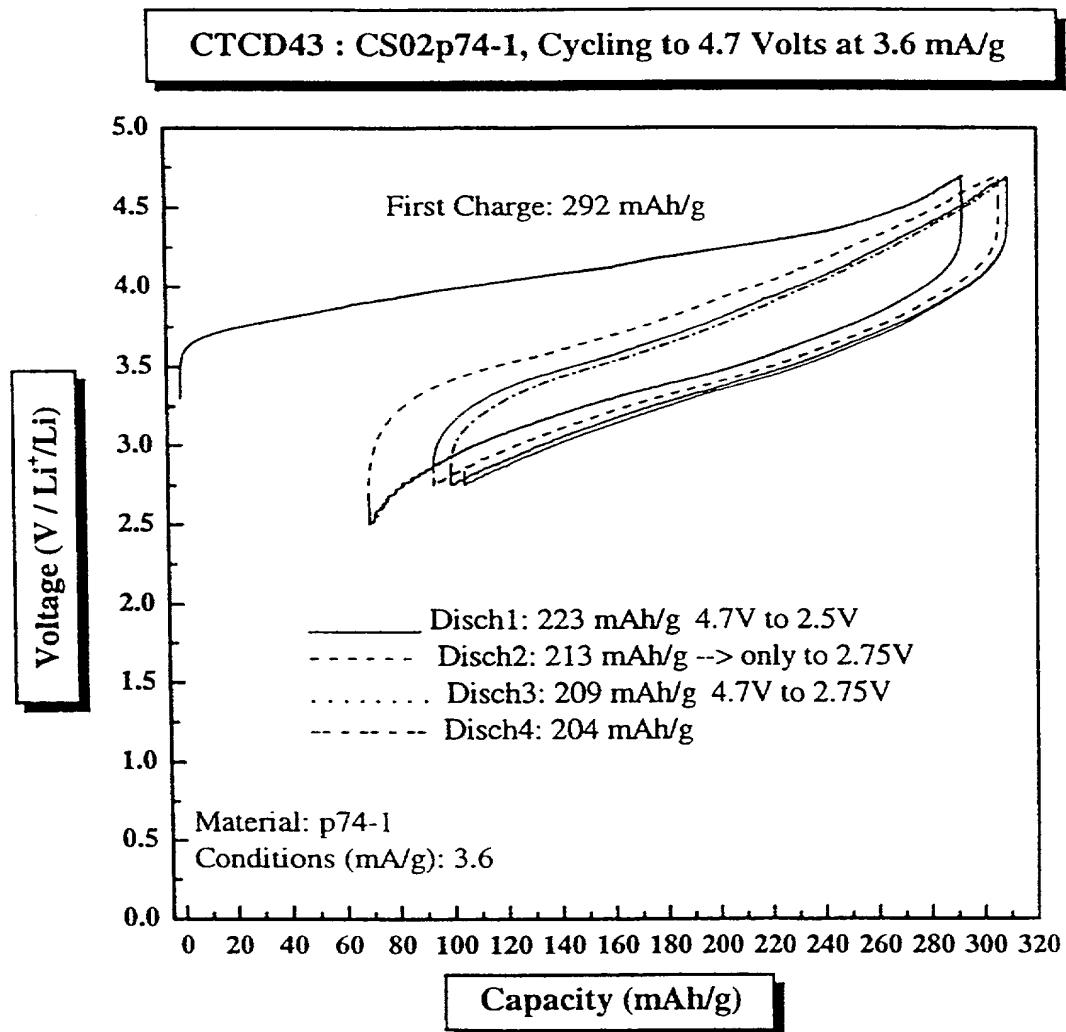


Figure 9

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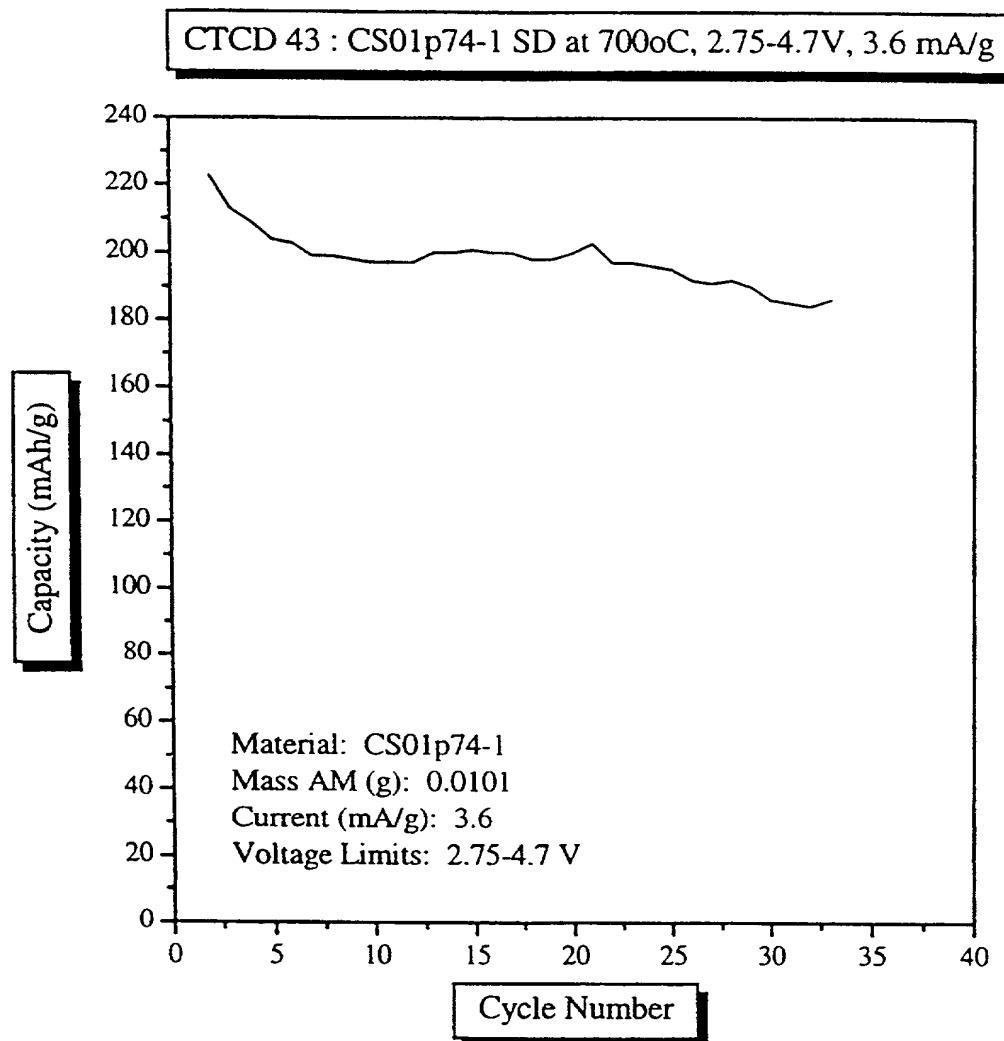


Figure 10

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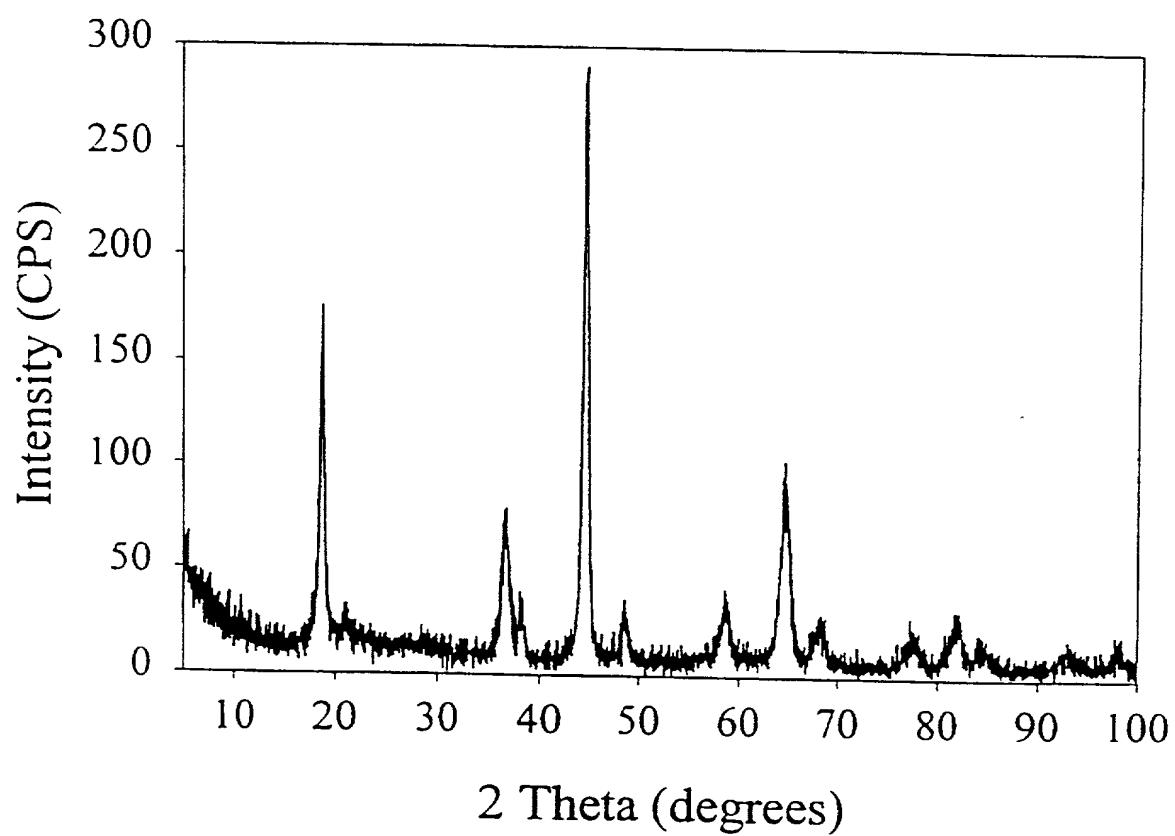


Figure 11

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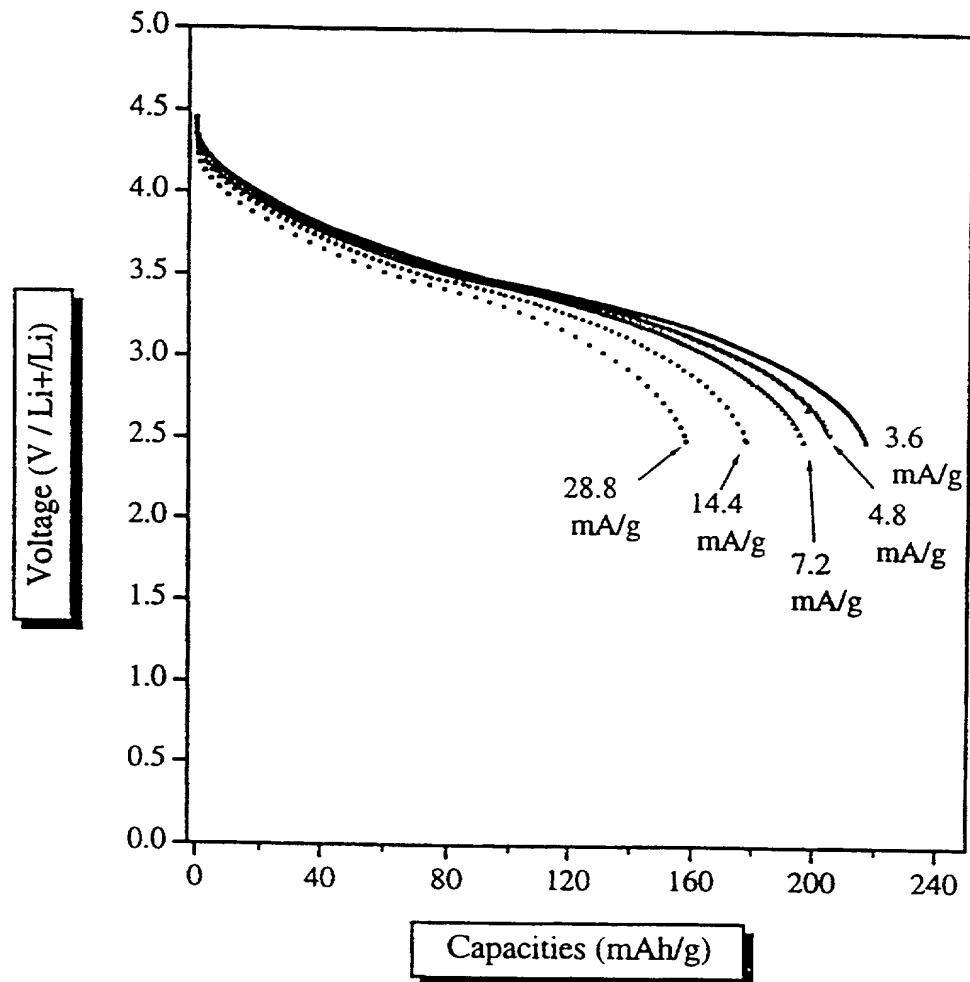


Figure 12

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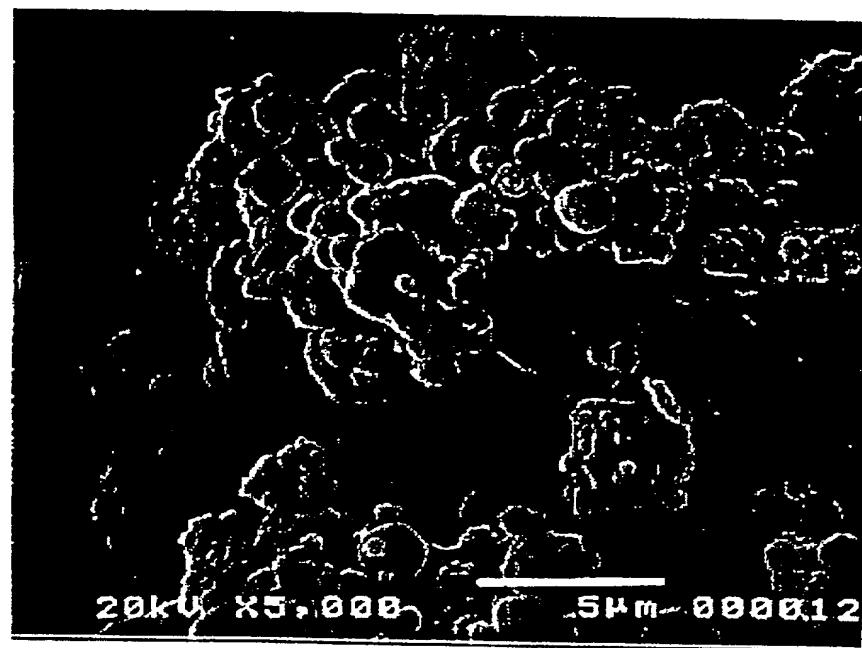
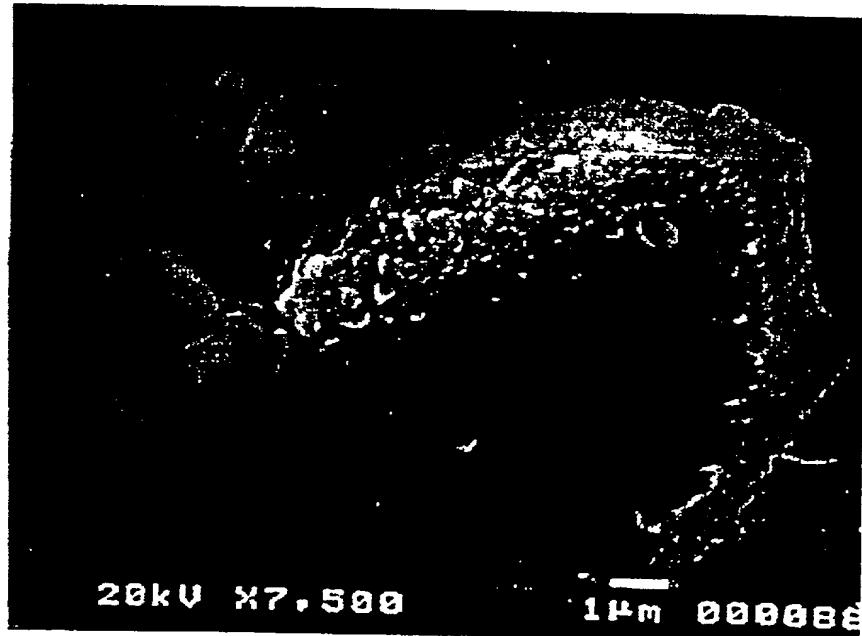


Figure 13

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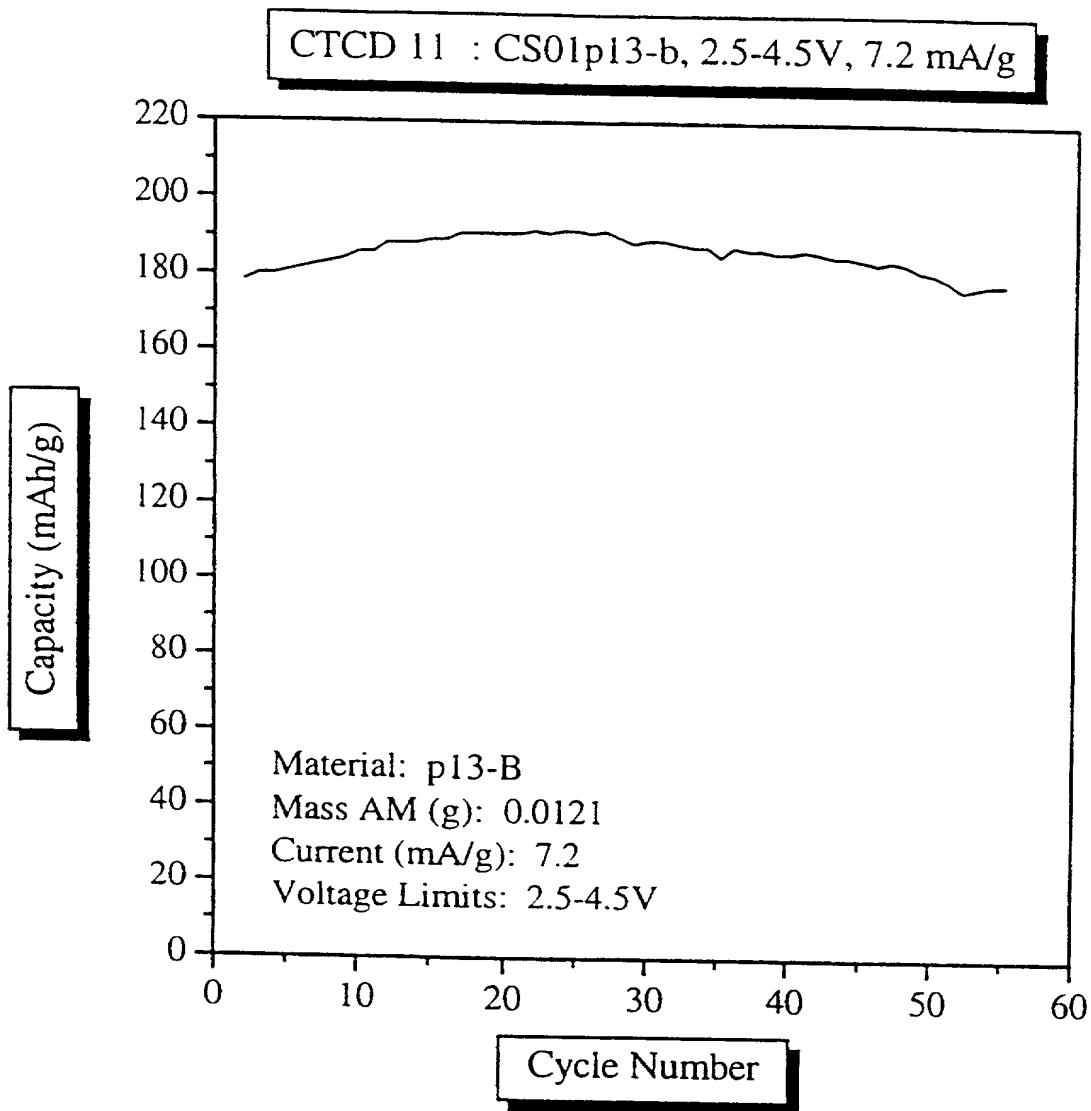


Figure 14

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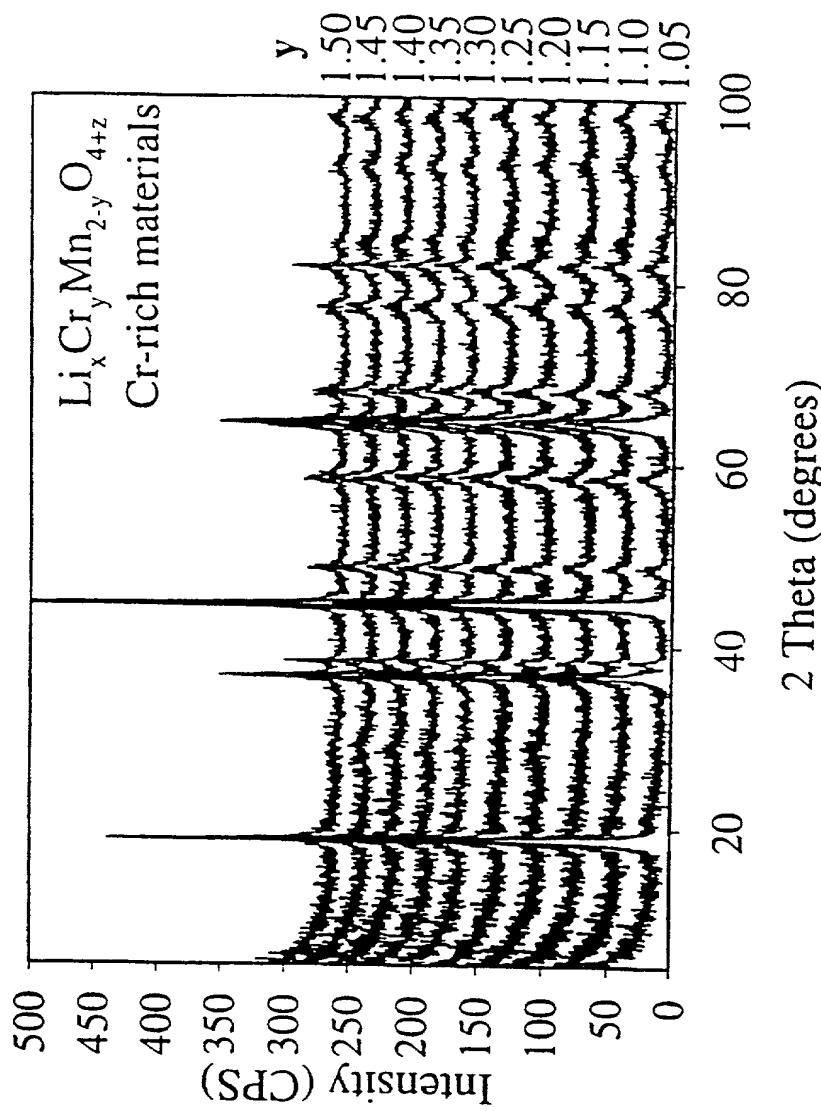


Figure 15

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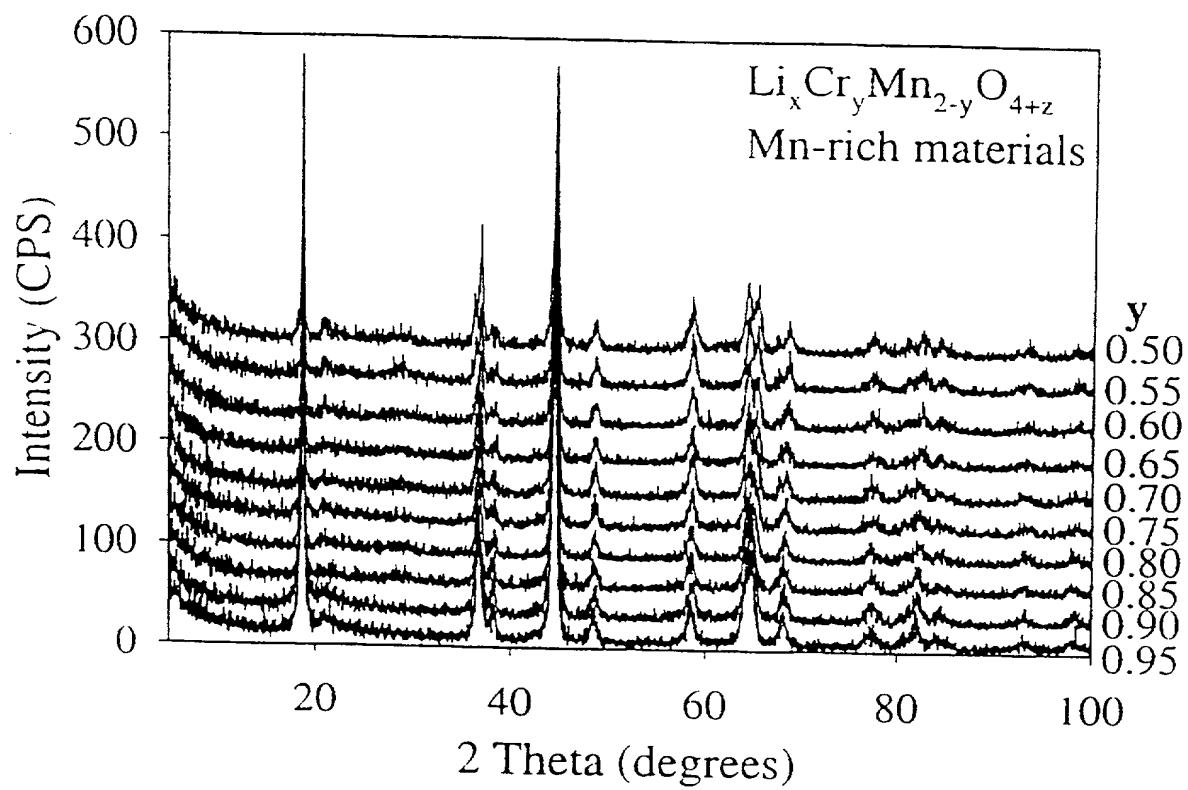


Figure 16

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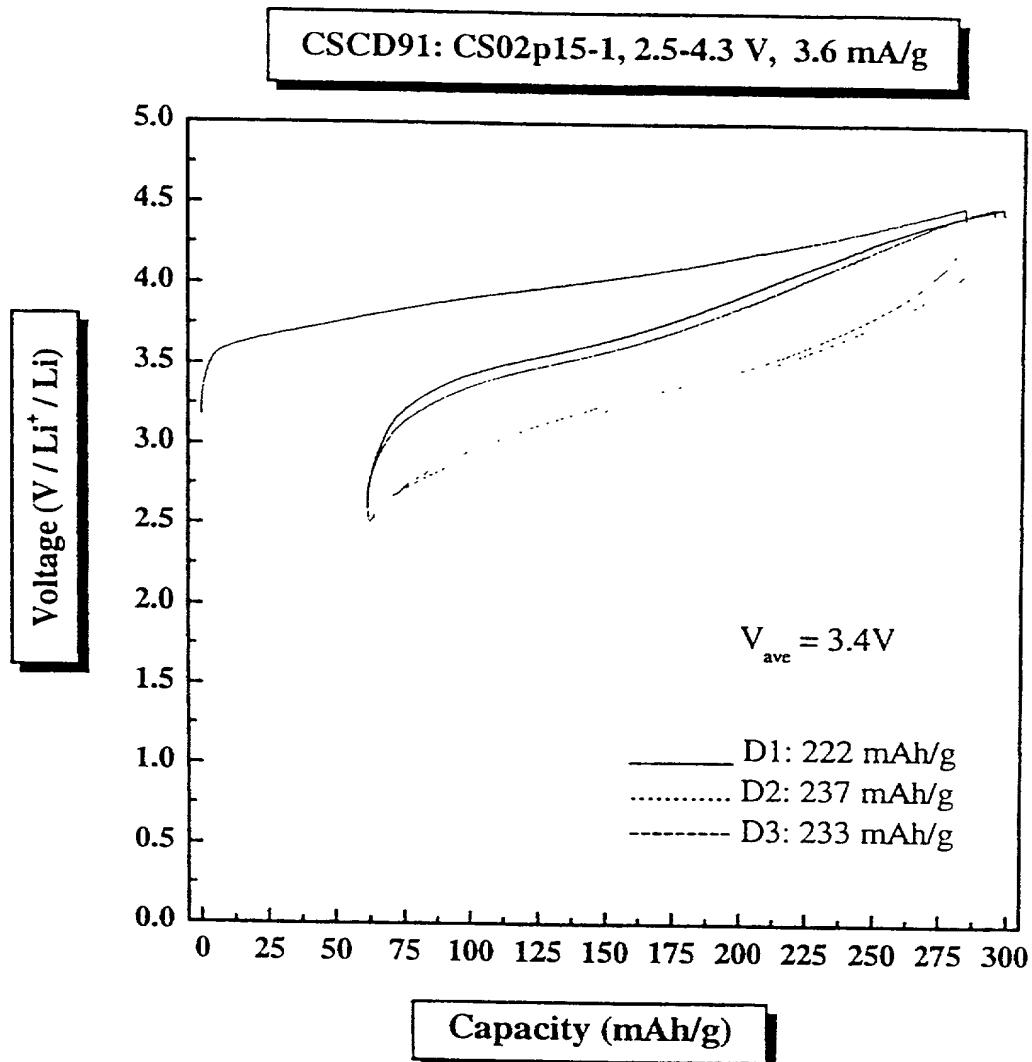


Figure 17

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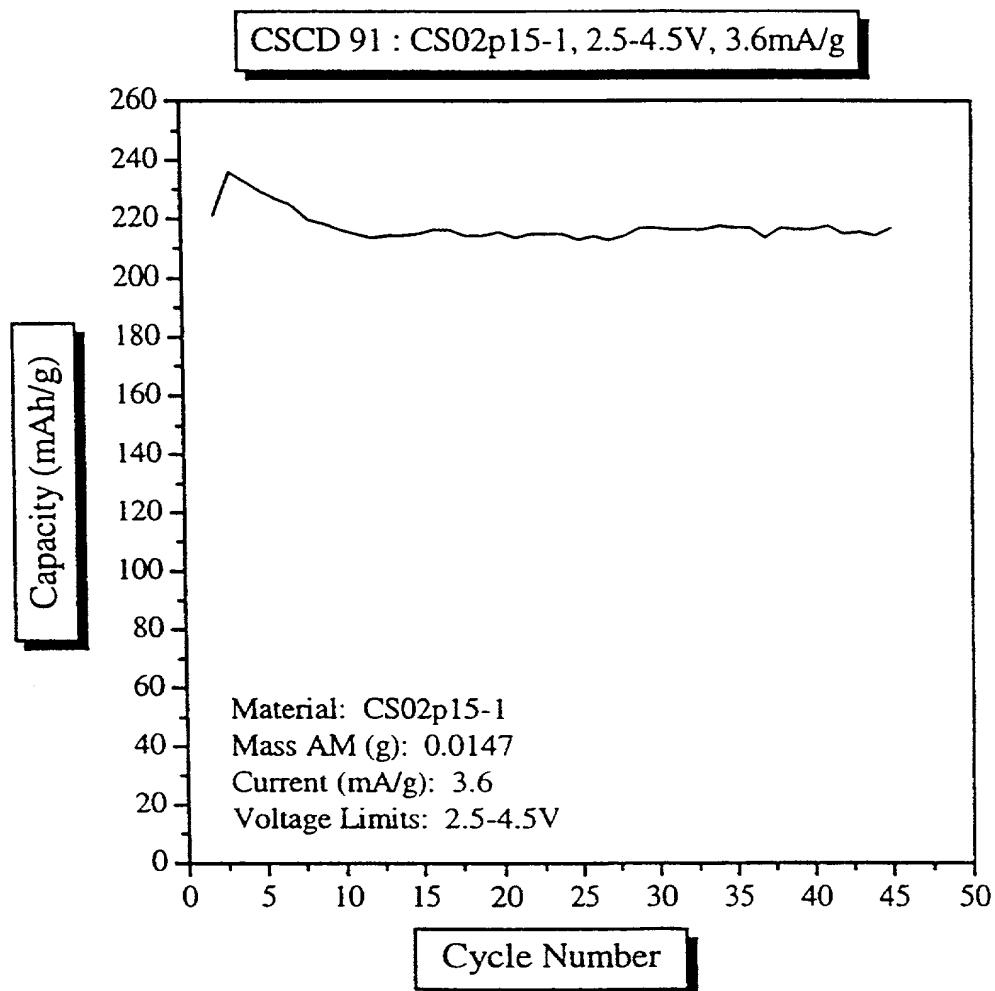


Figure 18

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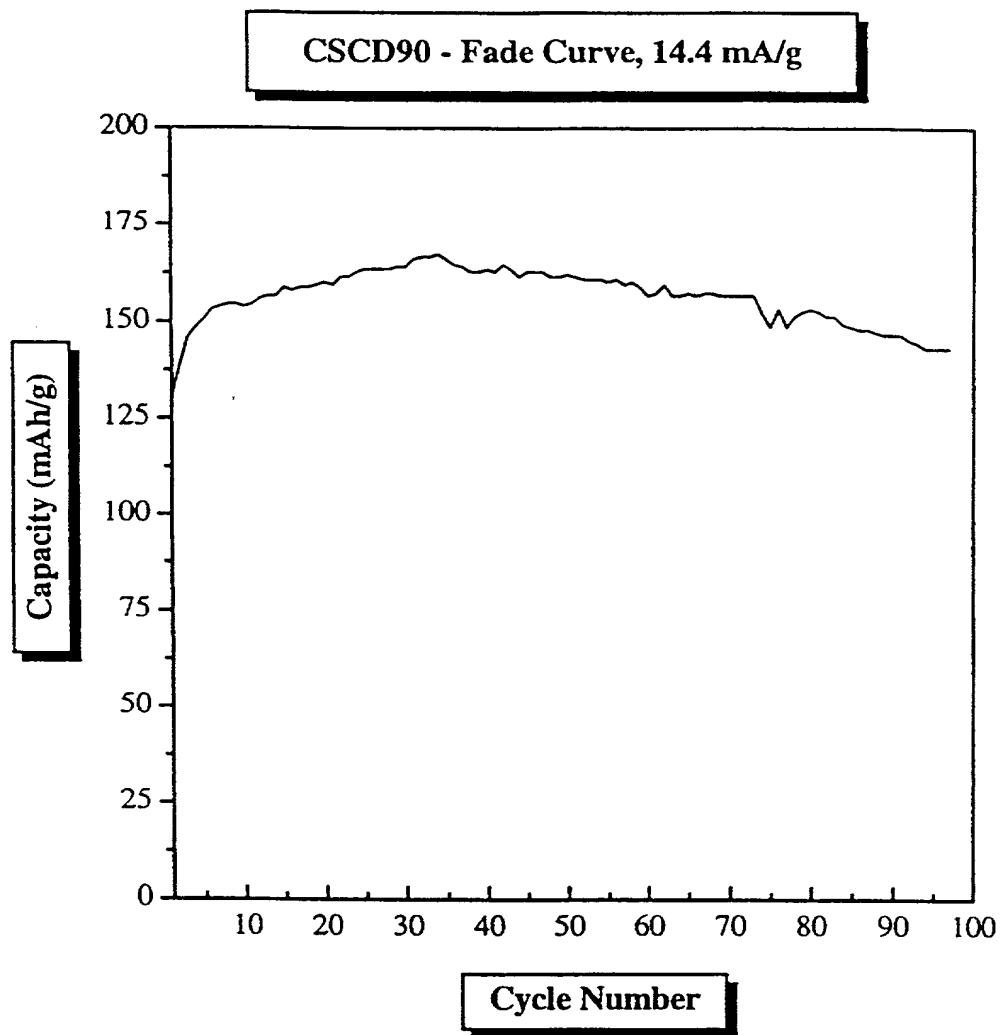


Figure 19

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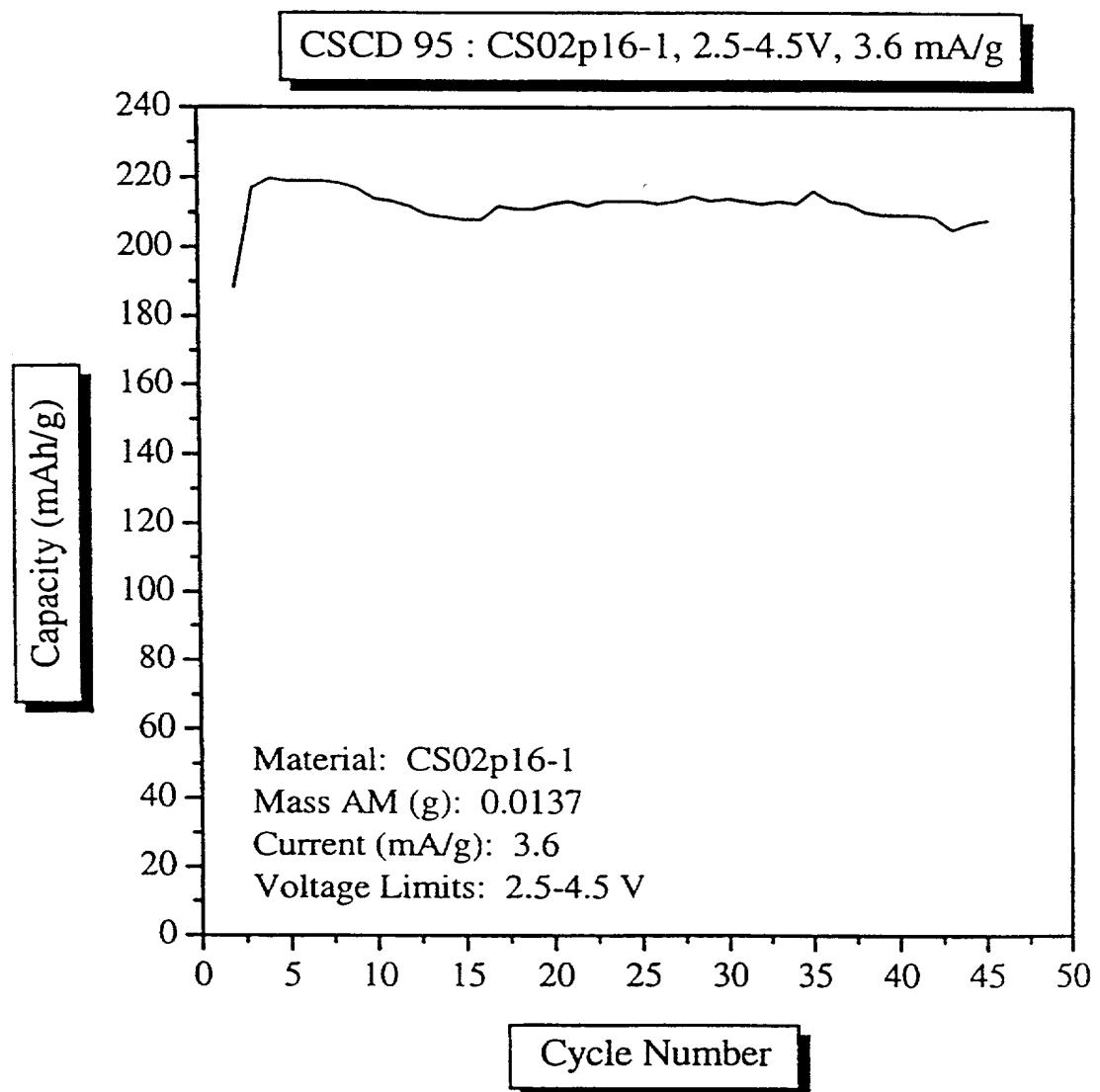


Figure 20

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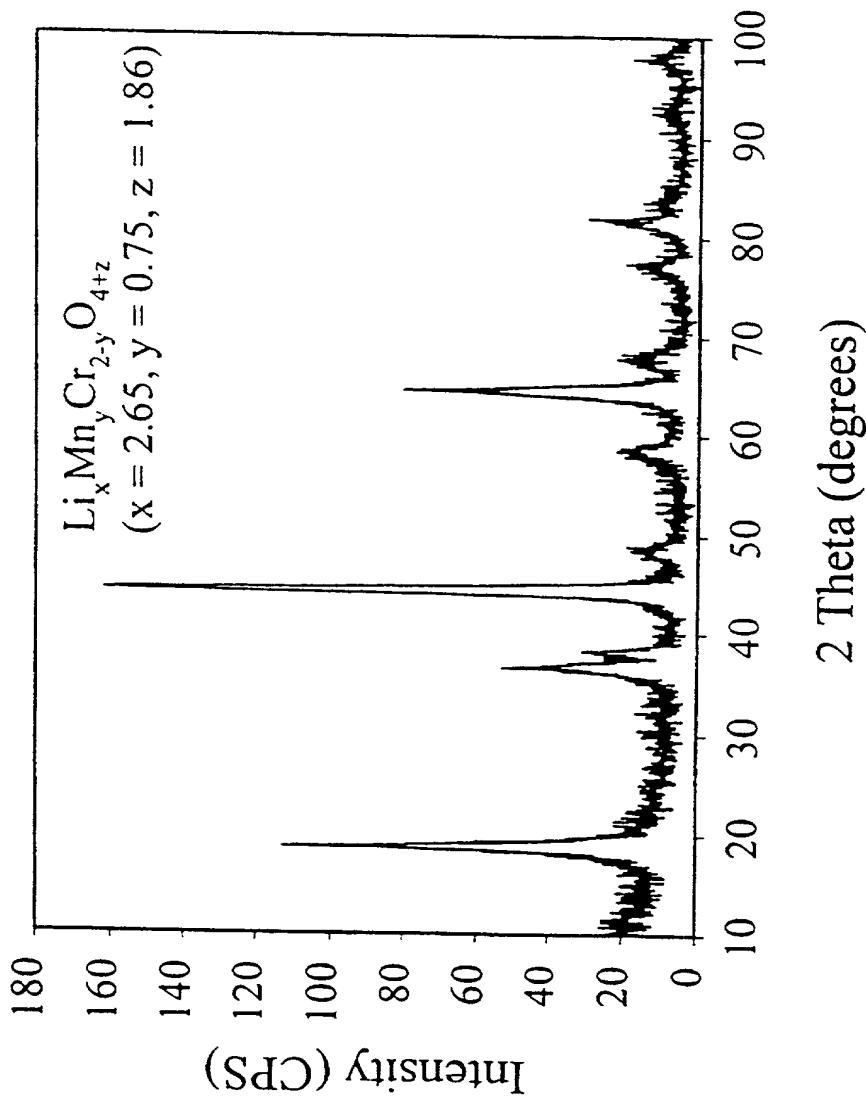


Figure 21

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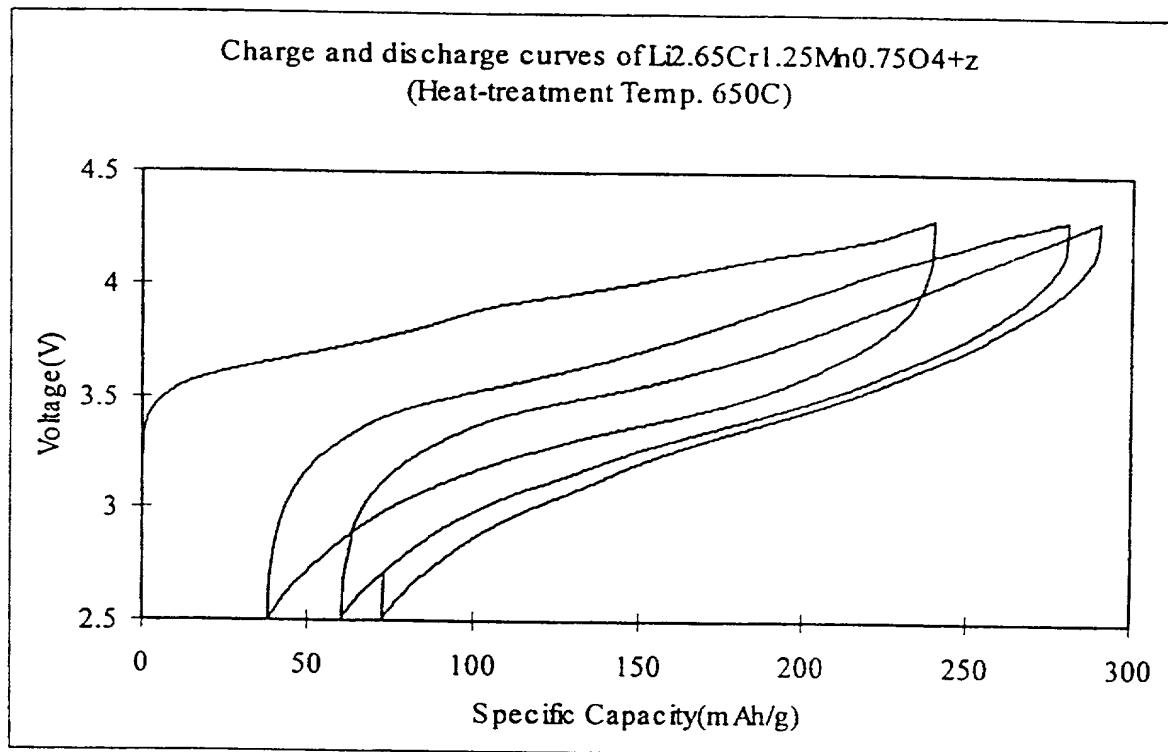


Figure 22

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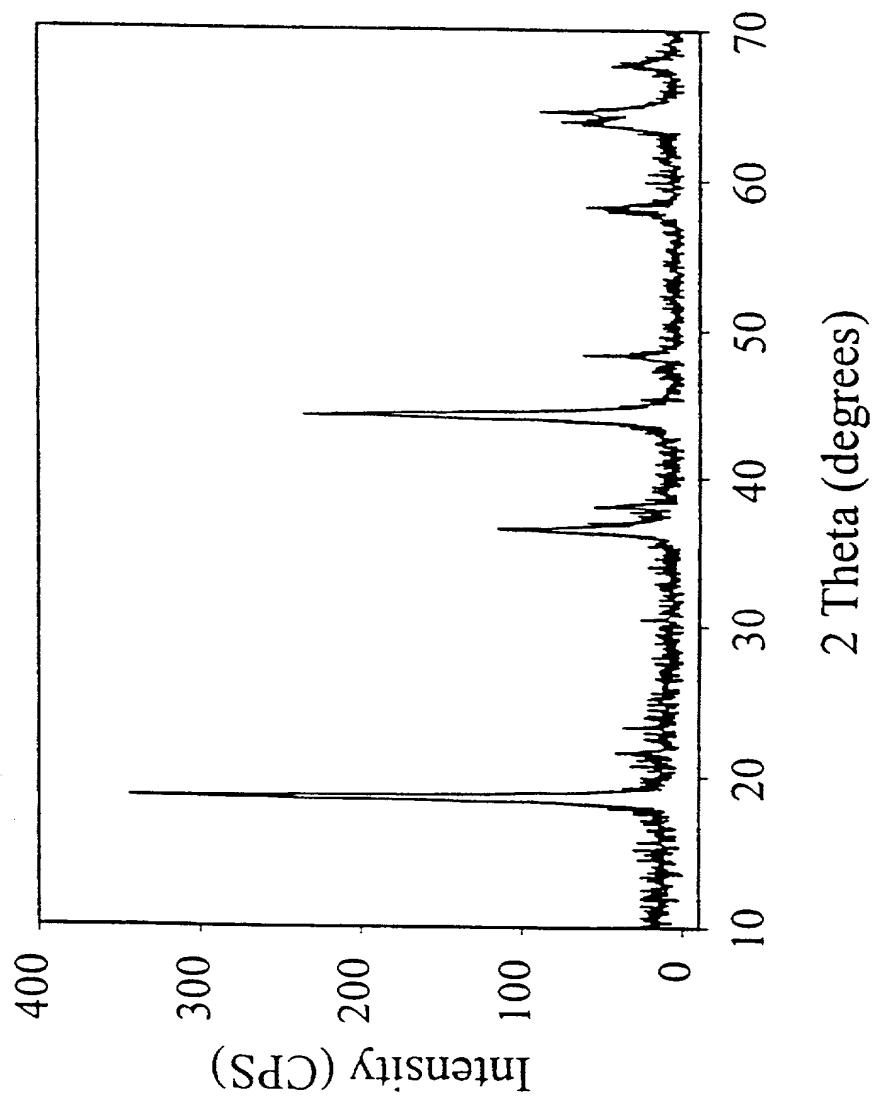


Figure 23

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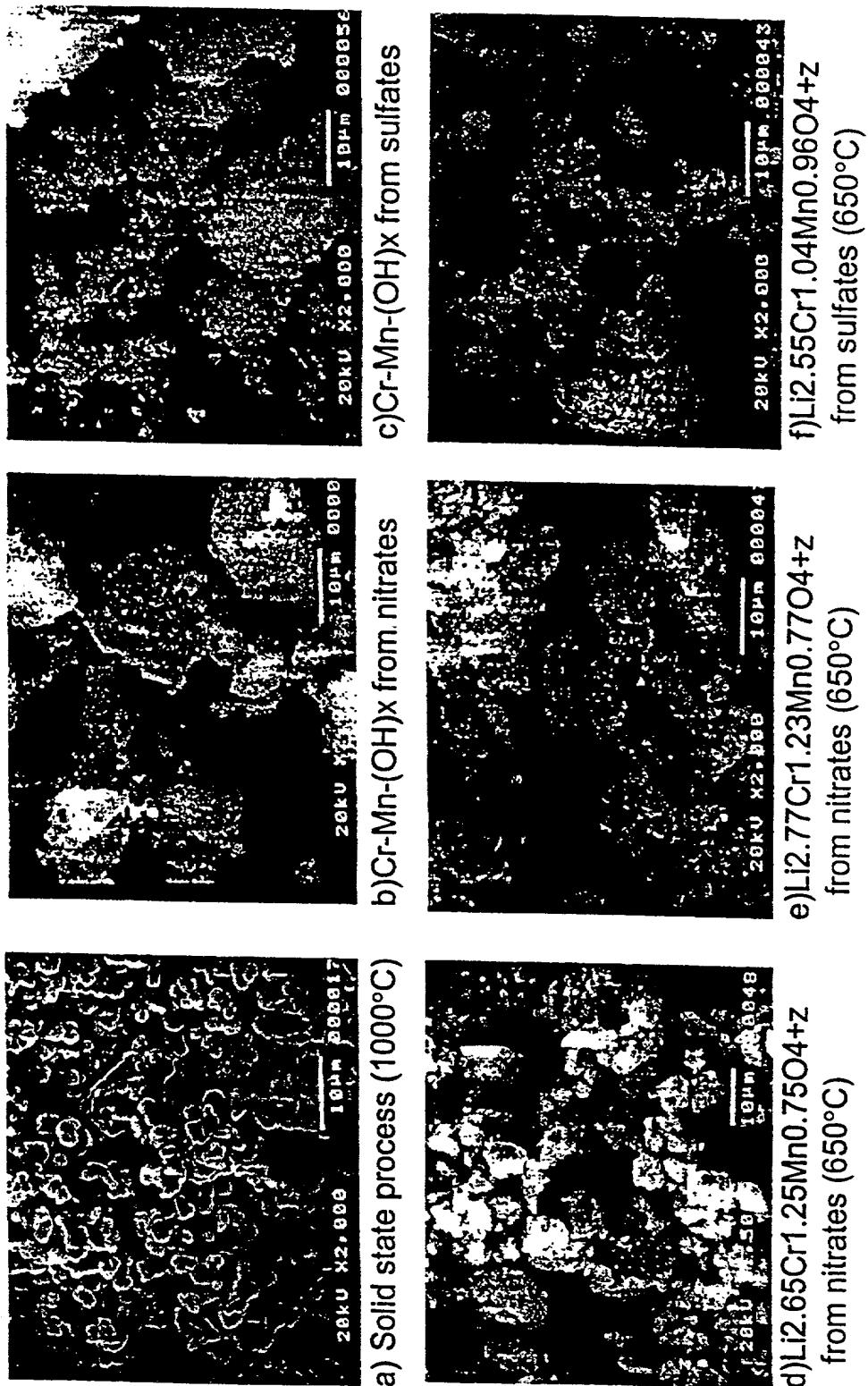
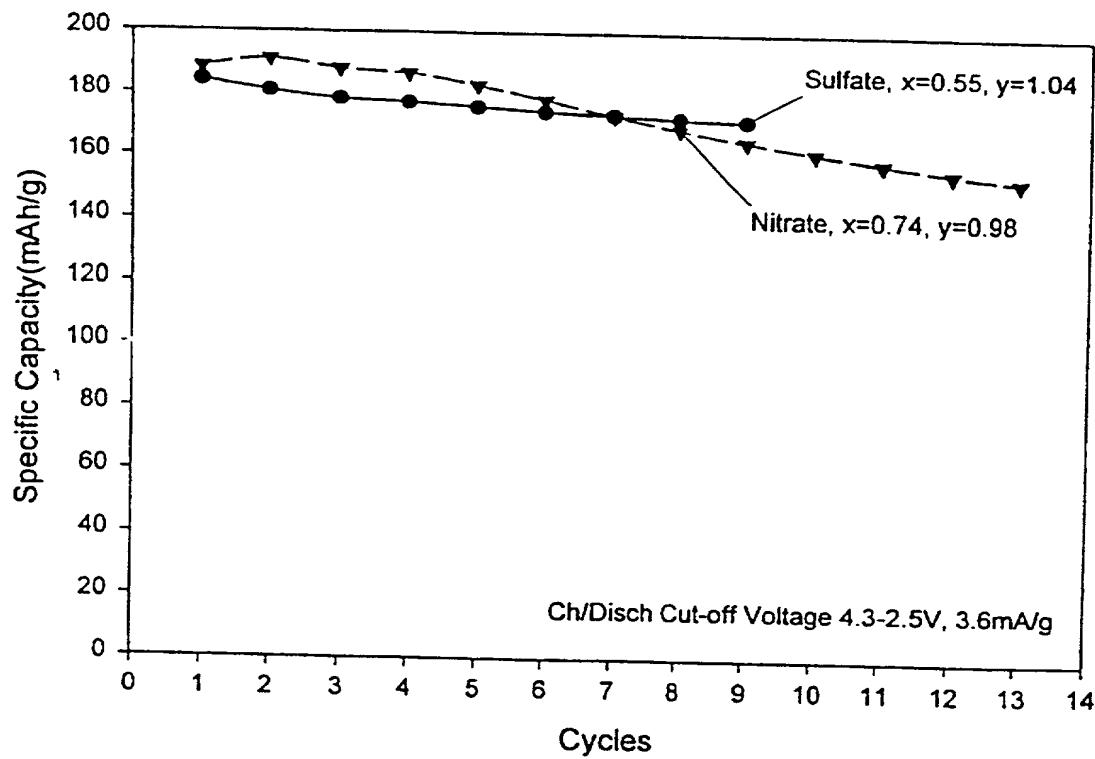


Figure 24

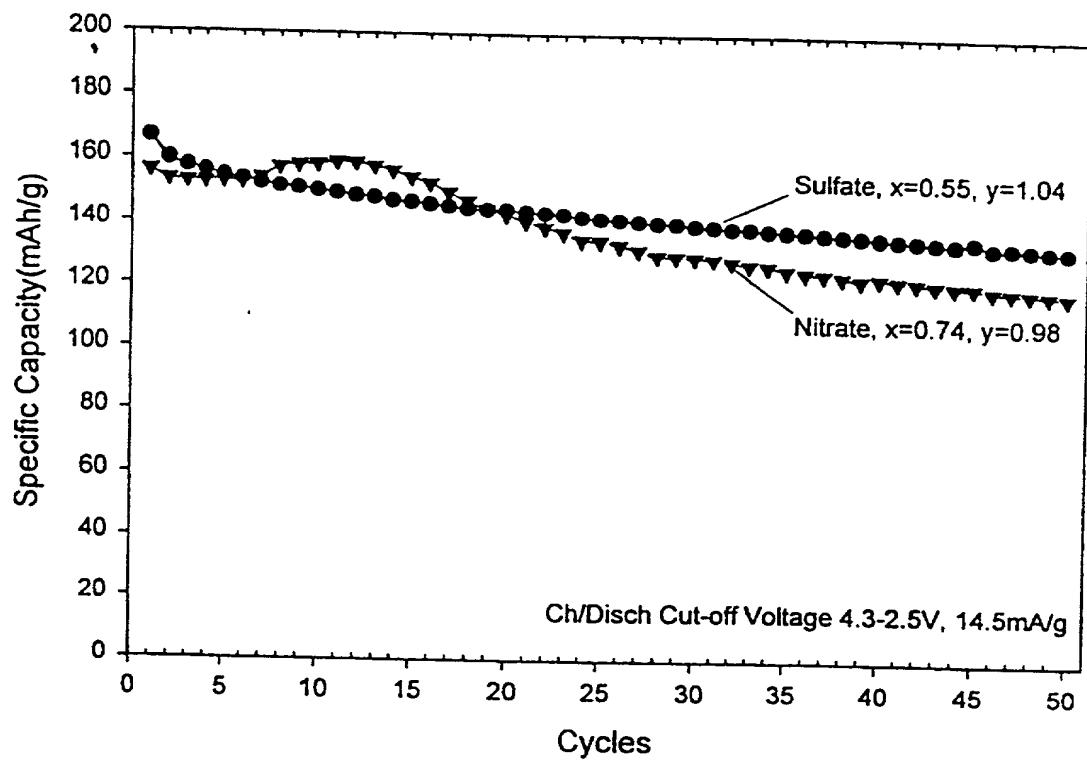
25/26



Specific capacity at 3.6 mA/g of  $\text{Li}_{2+x}\text{Cry}\text{Mn}_{2-y}\text{O}_{4+z}$  samples prepared by the co-precipitation process from indicated metal salts.

Figure 25

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Specific capacity at 14.5 mA/g of  $\text{Li}_{2+x}\text{Cr}_y\text{Mn}_{2-y}\text{O}_4+z$  samples prepared by the co-precipitation process from indicated metal salts.

Figure 26

## DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below), or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled "CATHODE ACTIVE MATERIAL FOR LITHIUM ELECTROCHEMICAL CELLS" the specification of which

is attached hereto

was filed on June 11, 2001 as Application Serial No. 09/857,701.

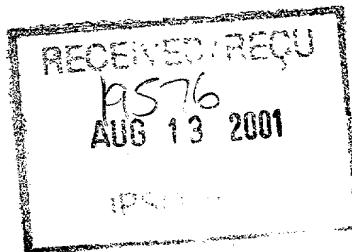
was filed as PCT international application Number PCT/CA00/00194 on February 28, 2000 and was amended under PCT Article 19 on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or (f), or 365(b) of any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent, inventor's or plant breeder's rights certificate(s), or any PCT international application having a filing date before that of the application on which priority is claimed.

60/158,303 8 October 1999 Expired  
(Number) (Filing Date) (Status: patented, pending, abandoned)



## DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below), or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled "CATHODE ACTIVE MATERIAL FOR LITHIUM ELECTROCHEMICAL CELLS" the specification of which

is attached hereto

was filed on June 11, 2001 as Application Serial No. 09/857,701.

was filed as PCT international application Number PCT/CA00/00194 on February 28, 2000 and was amended under PCT Article 19 on \_\_\_\_\_ (if applicable).

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60/158,303    8 October 1999    Expired  
(Number)    (Filing Date)    (Status: patented, pending, abandoned)

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Inventor's signature \_\_\_\_\_

Date:

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Address all correspondence to:

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Intellectual Property Services Office  
EG-12, Bldg. M-58, Montreal Road  
Ottawa, Ontario, Canada  
K1A 0R6

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or any patent issued thereon.

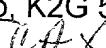
Full name of sole or first inventor: YOO, Yeong-Chang

Inventor's signature



Date: August 8, 2001

Residence: 164 Centrepointe Dr., Nepean, Ontario, K2G 5C2, Canada



Citizenship: Korea

Post Office Address: Same as Residence

Full name of second joint inventor, if any: SEUNG, Do-young

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Date:

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Ottawa, Ontario, Canada  
K1A 0R6

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor: YOO, Yeong-Chang

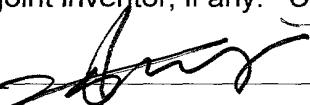
Inventor's signature \_\_\_\_\_ Date:

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20 Full name of second joint inventor, if any: SEUNG, Do-young

Inventor's signature  Date: *august 10. 2007*

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300 Full name of third joint inventor, if any: DAVIDSON, Isobel

Inventor's signature Isobel Davidson Date: August 8, 2001

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